

## **Responses to Comments**

on the Additional Investigation Results

National Aeronautics and Space Administration, Jet Propulsion Laboratory, Pasadena, California

December 2008

#### INTRODUCTION

In January 2007, the National Aeronautics and Space Administration (NASA) issued a technical memorandum¹ documenting the results of the additional investigation associated with the Remedial Investigation (RI) Addendum Work Plan². This study was performed as part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) program at NASA's Jet Propulsion Laboratory (JPL). Specifically, the objectives of the study were to (1) evaluate the downgradient (southern) extent of chemicals originating from the JPL facility and (2) determine if the occurrence of perchlorate in the Sunset Reservoir area was associated with migration from the JPL facility.

Upon release of the memorandum, NASA invited broad review and discussion of this study from the regulatory agencies who are parties to the Federal Facilities Agreement (FFA),<sup>3</sup> along with the City of Pasadena, Raymond Basin Management Board (RBMB), the Department of Public Health (DPH), and others. NASA received comments from the U.S. Environmental Protection Agency (EPA), California Department of Toxic Substances Control (DTSC), and the City of Pasadena (with support from their consultant, Geoscience Support Services, Inc.).

This document provides responses to these comments. First, an overall response to the five general (or overarching) categories of comments received from all reviewers is provided. The five general categories of comments include:

- 1. Applicability of the two groundwater models to chemical fate and transport, considering that the models were developed for water management (RBMB Model<sup>4</sup>) and plume containment (JPL Model<sup>5</sup>) and considering the potential for preferential pathways.
- 2. Evidence that the leading edge of NASA's perchlorate plume has been established.
- 3. Applicability of carbon tetrachloride as a tracer, considering concentrations, potential biological degradation, and sorption.
- 4. Oxidation-reduction (redox) conditions in the aquifer.
- 5. Perchlorate isotope data indicate there are multiple sources of perchlorate in the Basin, but alone may not eliminate JPL as a source in the Sunset Wells.

Second, we also provide responses to individual comments received from each agency. Responses to the comments from the EPA, DTSC, and City of Pasadena are provided as Attachments 1, 2, and 3, respectively.

<sup>&</sup>lt;sup>1</sup> NASA. 2007. Technical Memorandum Additional Investigation Results, National Aeronautics and Space Administration, Jet Propulsion Laboratory, Pasadena, California. Available At: <a href="http://jplwater.nasa.gov/NMOWeb/AI-TM/AI-TM.htm">http://jplwater.nasa.gov/NMOWeb/AI-TM/AI-TM.htm</a>. January.

<sup>&</sup>lt;sup>2</sup> NASA. 2004. *Operable Unit 3 Remedial Investigation (RI)* Addendum Work Plan (Pasadena Sampling Plan [PSP]-2004-1). Prepared by Battelle for the National Aeronautics and Space Administration. November.

<sup>&</sup>lt;sup>3</sup> United States Environmental Protection Agency, Region 9 and the California State Department of Toxic Substances Control and the California Regional Water Quality Control Board and the National Aeronautics and Space Administration. 1992. *Federal Facilities Agreement Under CERCLA Section 120 for the Jet Propulsion Laboratory*. December.

<sup>&</sup>lt;sup>4</sup> Geoscience. 2004. Technical Memorandum Raymond Basin Ground Water Flow Model Predictive Simulations. December.

<sup>&</sup>lt;sup>5</sup> NASA. 2003. *JPL Groundwater Modeling Report*. December.

#### **SUMMARY OF APPROACH**

NASA's approach to achieving the objectives of the Additional Investigation was to evaluate all of the available data in an integrated manner. NASA evaluated four lines of evidence, representing all of the available data, to establish a conceptual site model for the study area and achieve the objectives of the study. The four lines of evidence included groundwater modeling data, groundwater geochemical data, chemical concentration data collected as part of the JPL groundwater monitoring program, and perchlorate isotope analysis data. Each of the four lines of evidence provide important information and need to be evaluated in an integrated fashion to fully understand the complexities of underground conditions and the presence of perchlorate in local groundwater. In responding to the comments received, we have attempted clarify how the information from the four lines of evidence stands up together.

## GENERAL COMMENT 1: APPLICABILITY OF THE TWO GROUNDWATER MODELS TO CHEMICAL FATE AND TRANSPORT

Several comments were received regarding the potential applicability of the two groundwater models to chemical fate and transport, considering that the models were developed for water management (RBMB Model) and plume containment (JPL Model), and considering the potential existence of preferential pathways. The reason why the JPL Model (a model developed to evaluate plume containment) is appropriate for evaluating groundwater flow paths near JPL is that drinking water production wells operating in the Monk Hill Subarea since the early 1900s (that are included in the model) have provided containment of groundwater beneath JPL. The JPL Model is more appropriate than the RBMB Model for evaluating plume containment in the Monk Hill Subarea because it was designed specifically for that purpose, having finer model resolution in the Monk Hill Subarea and near the production wells. The RBMB Model was not developed to evaluate plume containment, but to understand general groundwater transport within the Basin and evaluate various conjunctive use scenarios. Even so, the groundwater flow paths in the Monk Hill Subarea generated by the RBMB Model appear to be consistent with the JPL Model.

To further ensure applicability, NASA compared the modeling approach utilized for the JPL groundwater modeling effort to the EPA's guidance for evaluating capture zones.<sup>6</sup> This comparison is documented as part of the responses to comments from EPA (Attachment 1) and demonstrates that the JPL Model was developed consistent with EPA guidance, providing an accurate understanding of capture zones.

As part of the Additional Investigation, the average extraction rates between 1960 and 2000 were used to evaluate capture zones using the JPL Model. This timeframe is believed to be most appropriate given our understanding of when the chemicals were historically released and projected travel times. Perchlorate used during testing at JPL in the mid-1940s and 1950s would have traveled from seepage pits through almost 200 feet of vadose zone and in groundwater approximately 2,500 feet to the closest production well, the Arroyo Well. Conservative estimates indicate vadose zone travel times of at least 7.5 years and travel times in groundwater of approximately 11 years.<sup>2</sup> As a result, considering average extraction rates between 1960 and 2000 provides an appropriate evaluation timeframe. Historical pumping records indicate that there are no significant periods of time since 1960 that City of Pasadena and Lincoln Avenue Water Company (LAWC) wells in the Monk Hill Subarea were not operational other than the 1985 to 1990 time period of minimal operation discussed in the Additional Investigation Technical Memorandum (see Figure R1). Therefore, based on the JPL Model, these wells provided effective containment of groundwater originating from JPL over the past 50 years.

<sup>&</sup>lt;sup>6</sup> U.S. EPA. 2008. *A Systematic Approach to the Evaluation of Capture Zones at Pump and Treat Systems*. EPA 600/R-08/003. Office of Research and Development. National Risk Management Research Laboratory. January.

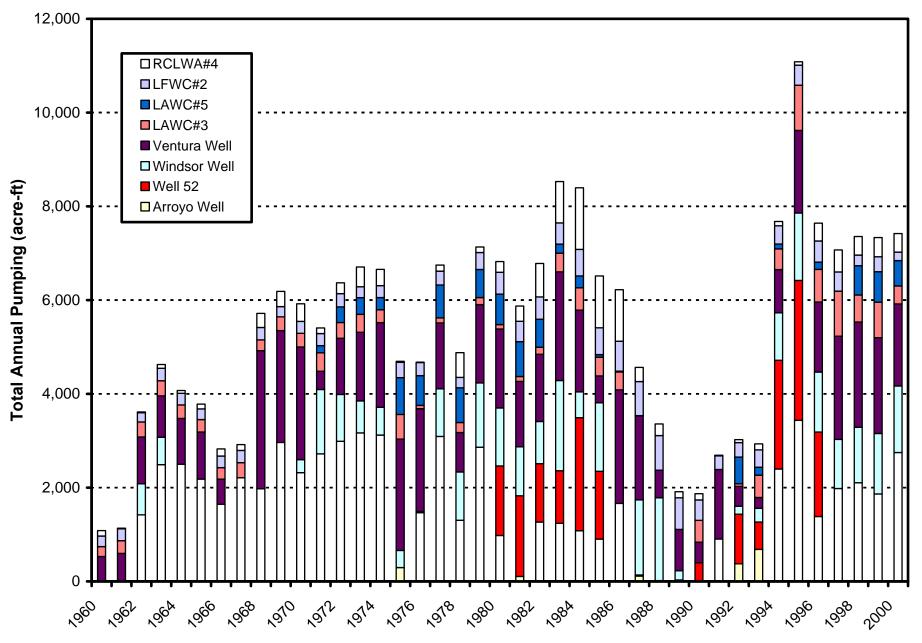


Figure R1. Groundwater pumping records from production wells in the Monk Hill Subarea since 1960 support NASA's assertion that these wells contained the perchlorate plume originating from JPL.

# GENERAL COMMENT 1: APPLICABILITY OF THE TWO GROUNDWATER MODELS TO CHEMICAL FATE AND TRANSPORT (CONT.)

While preferential pathways likely exist on a small scale near JPL due to the depositional environment in the Raymond Basin, these pathways do not affect the understanding of groundwater flow at the scale of this study (i.e., Sunset Reservoir wells are over three miles from JPL). Data collected during the RI,7 the JPL modeling effort, and the RBMB modeling effort indicate that groundwater flow is primarily controlled by the bedrock surface and pumping, not the current location of the Arroyo Seco stream bed, which is over 100 feet above the groundwater table near JPL. The bedrock surface (see Figure R2) channels groundwater flow southeast from JPL and then south as groundwater flows out of the Monk Hill Subarea. This flow pattern is exactly what is predicted by the JPL and RBMB groundwater models.

In addition, a large scale pumping test was performed as part of the JPL modeling effort and is documented as Appendix A in the JPL Modeling Report.<sup>5</sup> This test was completed to evaluate hydraulic properties of the hydrogeologic units in the vicinity of JPL. Analysis of the test data provided estimates of horizontal and vertical hydraulic conductivity, transmissivity, and storativity of the hydrogeologic units included in the JPL Model. As part of the aquifer test, data were collected from a network of shallow (MW-5, MW-8, MW-10, and MW-13) and multi-port (MW-3, MW-4, MW-12, and MW-17) monitoring wells as a series of three municipal production wells (Ventura, Windsor, and Well 52) were restarted after a period of shutdown.

The data from the aquifer test indicated that production well operation has a <u>significant effect</u> on groundwater flow, evidenced by the drawdown observed in monitoring wells at a distance of nearly 3,000 ft after one day of operation. Therefore, production well operation creates a considerable cone of depression with much higher hydraulic gradients than in static conditions, indicating pumping is a primary factor affecting groundwater flow in the Monk Hill Subarea. The pumping test also showed much higher drawdown (approximately 7 times higher) in the deeper aquifer layers where the production wells are screened. This variation in drawdown between aquifer layers led to the modeling of four separate layers in the JPL Model.

## GENERAL COMMENT 2: EVIDENCE THAT THE LEADING EDGE OF NASA'S PERCHLORATE PLUME HAS BEEN ESTABLISHED

Several other comments questioned whether NASA accomplished the first objective of the Additional Investigation — that is, to evaluate the downgradient (southern) extent of chemicals originating from the JPL facility. The Additional Investigation Technical Memorandum¹ defined the southern extent of the chemicals originating from the JPL facility by stating that the plume was contained in the Monk Hill Subarea. We now understand that this was confusing and a more specific definition is needed. NASA believes the first objective was accomplished and the downgradient extent of the plume has been established. Extensive monitoring data collected from four JPL monitoring wells in the Monk Hill Subarea, MW-20, MW-19, MW-21, and MW-26 (installed as part of the Additional Investigation),8 define the southern extent of the JPL perchlorate plume.

<sup>&</sup>lt;sup>7</sup> Foster Wheeler Environmental Corporation (FWEC). 1999. Final Remedial Investigation Report for Operable Units 1 and 3: On Site and Off-Site Groundwater. August.

<sup>&</sup>lt;sup>8</sup> NASA. 2008. *Technical Memorandum for Third Quarter 2008, Groundwater Monitoring Results*. Prepared by Battelle for the National Aeronautics and Space Administration. October.

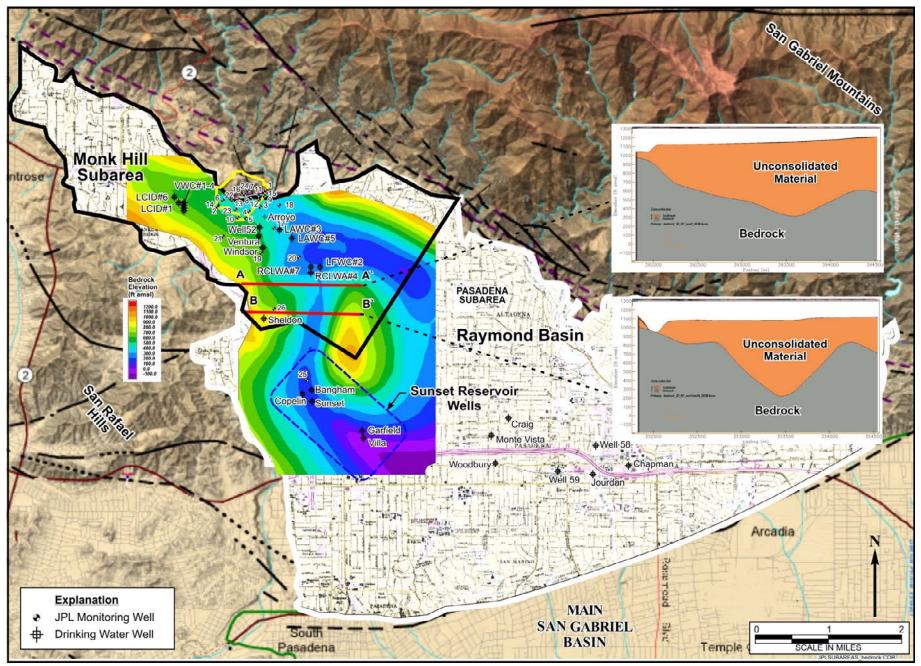


Figure R2. Groundwater pumping and the bedrock surface are the primary factors influencing groundwater flow paths in the Monk Hill Subarea. The bedrock valley shown on cross-section B-B' channels flow from the Monk Hill Subarea toward the Sunset Reservoir wells.

## **GENERAL COMMENT 2 (CONT.)**

MW-20 is located approximately 1 mile southeast of JPL. Sporadic detections of perchlorate have been observed in samples collected from MW-20 (Screen 4) since 1998 associated with deeper portions of the aquifer and Type 1 or 2 water quality (consistent with a source originating from JPL). Specifically, samples collected from MW-20 (Screen 4) contained perchlorate concentrations of 20  $\mu$ g/L, 30  $\mu$ g/L, 58.5  $\mu$ g/L, 124  $\mu$ g/L, and 24.2  $\mu$ g/L in October/November 1998, April/May 2002, October/November 2002, April/May 2003, and July/August 2008, respectively. It is believed that the detections in 1998, 2002, and 2003 were associated with the 1985-1990 shutdown of Arroyo Well, Well 52, LAWC#3, and LAWC#5. The July/August 2008 detection is being evaluated. These detections represent the furthest migration of perchlorate originating from JPL. Based on groundwater modeling, MW-20 is within the capture zone of Rubio Cañon Land and Water Association (RCLWA) wells, which are the most southeastern wells in the Monk Hill Subarea. The JPL Model shows that the groundwater near MW-20 is contained by the RCLWA wells and does not migrate to the Sunset Reservoir wells.

MW-19, MW-21, and MW-26 are located south of JPL but not as far east as MW-20. Perchlorate detected in these wells is not associated with JPL, but help define the southern extent of JPL perchlorate (see Figure R3):

- MW-19 is located to the south of the JPL facility near the City of Pasadena's Windsor Well. Low levels (less than  $10~\mu g/L$ ) of perchlorate have been detected in MW-19 (Screens 1 through 5); however, data indicate that these detections are not associated with JPL. Groundwater modeling shows that MW-19 is within the flow path of groundwater originating from sources cross-gradient and to the west of JPL. In addition, samples collected from MW-19 show a strong influence of imported water and have perchlorate concentrations that are comparable to the levels detected in the upgradient Valley Water Company (VWC) wells. Further, carbon tetrachloride has not been detected in MW-19 (except for an isolated detection in September 1996 at  $0.5~\mu g/L$  in Screen 4).
- MW-21 is located directly south of JPL and west of MW-19. Similar to MW-19, all available data indicate that perchlorate detections in MW-21 are not associated with JPL. Groundwater modeling shows that MW-21 is within the flow path of groundwater originating from sources cross-gradient and to the west of JPL. Carbon tetrachloride has not been detected in MW-21 and water quality in this well shows a strong influence of imported water.
- MW-26 is located approximately halfway between the JPL facility and the Sunset Reservoir wells and was installed in early 2005 as part of the Additional Investigation. Samples collected quarterly from MW-26 (Screen 1) between April 2005 and September 2007 did not contain perchlorate. Perchlorate was detected in October/December 2007 at 2.7 μg/L and January/February 2008 at 3.2 μg/L. These detections are not believed to be associated with JPL due to the absence of carbon tetrachloride combined with the presence of tetrachloroethylene (PCE), which is consistent with sources cross-gradient and to the west of JPL (i.e., La Cañada-Flintridge). In addition, MW-26 is within the flow path of groundwater originating cross-gradient to JPL. Samples collected from MW-26 (Screen 2) have not had detectable levels of perchlorate during quarterly monitoring.

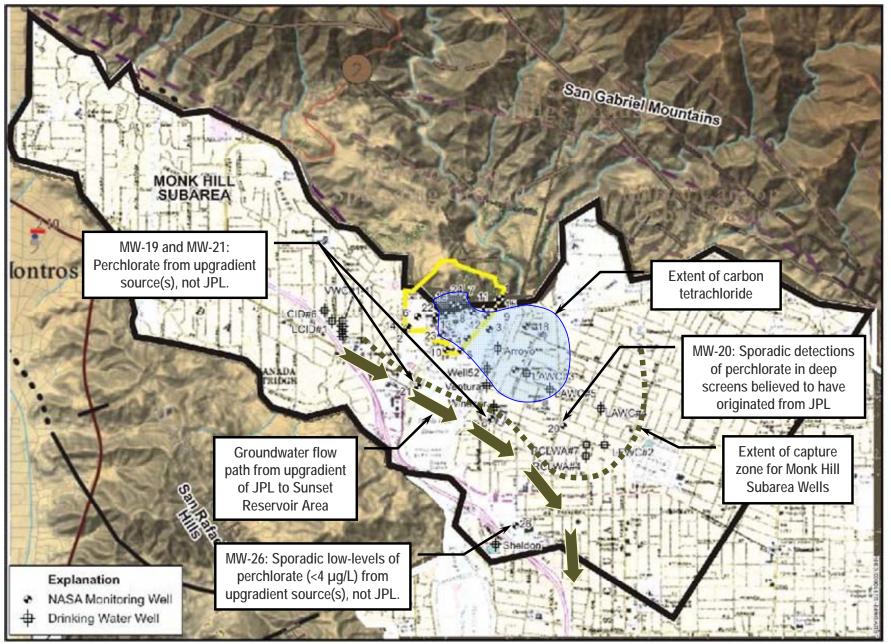


Figure R3. The southern extent of the JPL perchlorate plume is defined by MW-19, MW-20, MW-21, and MW-26; therefore, it is contained within the Monk Hill Subarea. Groundwater modeling and carbon tetrachloride data corroborate our understanding of extent of JPL perchlorate.

#### GENERAL COMMENT 3: APPLICABILITY OF CARBON TETRACHLORIDE AS A TRACER

Some comments questioned the applicability of carbon tetrachloride as a tracer for chemicals originating from JPL, considering relative concentrations, potential biological degradation, and differences in chemical properties impacting sorption to aquifer materials. NASA understands that in the absence of containment, perchlorate would likely travel more rapidly than carbon tetrachloride due to differences in their chemical properties (i.e., carbon tetrachloride will attach to organic matter in the aquifer matrix more readily than perchlorate). However, groundwater modeling and historical pumping records indicate that containment has occurred; therefore, it is possible to use carbon tetrachloride as an appropriate tracer. In addition, understanding the extent of carbon tetrachloride strengthens our understanding JPL's perchlorate plume because the carbon tetrachloride data support the groundwater modeling results and our understanding capture zones.

A strong correlation between perchlorate and carbon tetrachloride is observed at the JPL source area and as far downgradient as the LAWC wells, located approximately one mile from JPL. Figure R4 shows the carbon tetrachloride and perchlorate results in the two LAWC wells (LAWC#3 and LAWC#5) since the mid-1990s. These two wells are currently part of NASA's OU-3 response action<sup>9</sup> to contain the leading edge of the plume. At the LAWC wells, carbon tetrachloride concentrations are approximately one order of magnitude lower than perchlorate concentrations. However, the detection limit for carbon tetrachloride is also about one order of magnitude lower than the detection limit for perchlorate. Therefore, the use of carbon tetrachloride as a tracer is not limited by the relative concentrations between it and perchlorate.

Lastly, NASA's analysis recognized that biotic and abiotic carbon tetrachloride degradation requires an anaerobic environment. Groundwater data collected from the JPL monitoring network provide strong evidence that an anaerobic environment capable of degrading carbon tetrachloride is not present. These data include dissolved oxygen (DO) levels near saturation, nitrate levels generally greater than 1 mg/L as NO<sub>3</sub>, oxidation-reduction potential (ORP) readings generally above 100 mV, the general absence of ferrous iron, and the absence of evidence of anaerobic degradation of trichloroethylene (TCE) or PCE within the JPL chemical plume. The presence of chloroform, a daughter product of carbon tetrachloride degradation, cannot be used to indicate anaerobic degradation of carbon tetrachloride since chloroform was a compound used during historic laboratory operations at JPL¹² and is a disinfection byproduct. Therefore, anaerobic degradation of carbon tetrachloride does not limit its use as a tracer for chemicals originating from JPL.

<sup>&</sup>lt;sup>9</sup> NASA. 2007. *Final Interim Record of Decision for Operable Unit 3, Off-Facility Groundwater*. National Aeronautics and Space Administration, Jet Propulsion Laboratory, Pasadena, CA. August.

<sup>&</sup>lt;sup>10</sup> Doong R.A. and S.C. Wu 1992. "Reductive Dechlorination of Chlorinated Hydrocarbons in Aqueous Solutions Containing Ferrous and Sulfide ions." *Chemosphere* 24:1063-1075.

<sup>&</sup>lt;sup>11</sup> Interstate Technology and Regulatory Council (ITRC). 2005. A Systematic Approach to In Situ Bioremediation in Groundwater Including Decision Trees on In Situ Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate. Technology/Regulatory Guidelines ISB-8.

<sup>&</sup>lt;sup>12</sup> Foster Wheeler Environmental Corporation. 1999. *Final Remedial Investigation Report for Operable Unit 2: Potential On-Site Contaminant Source Areas*. National Aeronautics and Space Administration, Jet Propulsion Laboratory, Pasadena, CA. November.

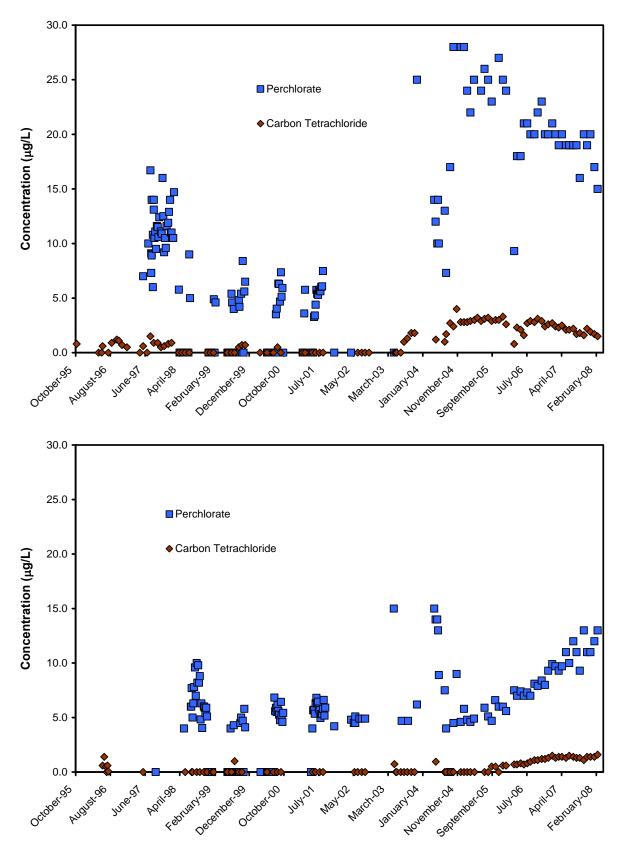


Figure R4. Perchlorate and carbon tetrachloride results in LAWC#3 (top) and LAWC#5 (bottom), which are located near the leading edge of the JPL plume, support the connection between these two chemicals and the applicability of carbon tetrachloride as a tracer for chemicals originating from JPL.

#### GENERAL COMMENT 4: OXIDATION-REDUCTION CONDITIONS IN THE AQUIFER

Some comments questioned NASA's assertion that the redox conditions in the aquifer are generally aerobic. The DO concentrations and ORP readings in the groundwater samples were used as the primary means of determining the redox conditions. The combination of the other terminal electron acceptors, such as nitrate, perchlorate, and ferrous iron, was used to support our understanding of aquifer redox conditions. Evaluation of these data provides strong evidence that the aquifer is in fact aerobic. DO levels in samples collected as part of the additional investigation were near saturation and ORP values were generally greater than 100 mV, indicating aerobic conditions. The only exceptions were in Screens 4 and 5 of MW-20, which showed negative ORP and some sulfide (although, DO levels indicated aerobic conditions). If anaerobic conditions sufficient to reduce sulfate do exist in deeper groundwater near MW-20, this would have a positive result, as perchlorate reducing conditions would also likely exist.

In addition to the DO levels and ORP values, other data supporting aerobic conditions in the aquifer include the general absence of ferrous iron, elevated concentrations of nitrate and perchlorate, the absence of PCE and TCE degradation daughter products within the JPL plume boundary, and the perchlorate isotope data, which do not support perchlorate degradation in the Monk Hill Subarea. As indicated previously, the presence of chloroform alone cannot be used to indicate anaerobic degradation of carbon tetrachloride since chloroform was a compound used during historic laboratory operations and is a disinfection byproduct.

## GENERAL COMMENT 5: PERCHLORATE ISOTOPE DATA MAY NOT ELIMINATE JPL AS A SOURCE IN THE SUNSET WELLS

The last general grouping of comments was associated with the perchlorate isotope data. EPA and DTSC concurred with NASA's interpretation that the perchlorate isotope data indicate multiple sources of perchlorate in the Basin, but questioned whether the isotope data eliminated JPL as a source in the Sunset Reservoir wells.

During the Additional Investigation, samples from three of the five Sunset Reservoir wells, including Bangham Well, Garfield Well, and Sunset Well, were analyzed for perchlorate isotope composition. Bangham Well and Garfield Well isotopic data cannot be explained by mixing of JPL perchlorate and other sources (see Figure R5), as their <sup>18</sup>O composition is much heavier than JPL and both appear to have a significant contribution from natural/fertilizer perchlorate.

Upon initial evaluation, it might appear that the perchlorate in groundwater collected from the Sunset Well is a mixture of JPL perchlorate and other sources. NASA's conclusion that Sunset Well does not contain JPL perchlorate is supported by isotope data from MW-19 (Screen 2), which is isotopically indistinguishable from that from the Sunset Well. Since MW-19 is a JPL monitoring well, much is known about this well, including that the source of perchlorate in MW-19 (Screen 2) did not originate from JPL. We know that carbon tetrachloride has never been detected in MW-19 (Screen 2) even though it is less than a mile from JPL. This is because MW-19 is cross-gradient from JPL (i.e., not within the flow path of groundwater originating from JPL). In addition, tritium data indicate recently recharged water at this well location, which is consistent with injection of imported water upgradient of MW-19 in the Valley Water Company wells. Also, groundwater modeling indicates that groundwater cross-gradient and to the west of JPL flows past MW-19 and on toward the Sunset Reservoir wells. Therefore, MW-19 (Screen 2) and the Sunset Well may contain perchlorate from the same source, but not from JPL.

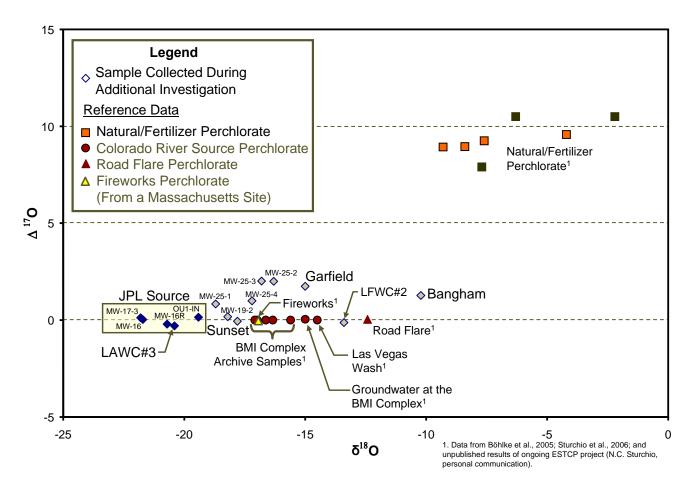


Figure R5. The perchlorate isotopic signature in groundwater collected at the Garfield Well and Bangham Well cannot be explained via mixing with the JPL perchlorate. Data indicate that the groundwater collected from the Sunset Well does not represent a mixture of other perchlorate sources and a JPL source due to its similarity to perchlorate in MW-19 (Screen 2), which is not from JPL.

## **CONCLUSIONS**

NASA's conceptual site model for the JPL perchlorate plume is based on available data analyzed in an integrated fashion. We maintain that the four lines of evidence presented in the Additional Investigation Technical Memorandum¹ must be evaluated together to fully understand the complexities of underground conditions and the presence of perchlorate in local groundwater. When this is done, the data support that the extent of perchlorate originating from JPL is contained within the Monk Hill Subarea, with MW-20 representing the southeastern extent of the plume. In summary, the data provide a compelling picture that perchlorate originating from JPL has not reached the Sunset Reservoir wells.

Figure R6 summarizes the results of the four lines of evidence presented in the Additional Investigation Technical Memorandum.<sup>1</sup> These data comprise NASA's conceptual site model for the JPL perchlorate plume. The conceptual site model confirms JPL as the source of perchlorate at several wells, including MW-16, MW-17-3, and LAWC#3. At other locations, including the Sunset Reservoir wells, the conceptual site model supports a source other than JPL. Any alternative conceptual site model would need to be corroborated with all available data, and stand up in cases where JPL perchlorate is the source and where it is not.

Well	Distance From JPL Source Area (Feet)	Groundwater Geochemistry od	Groundwater <b>si</b> Modeling <b>dd</b>	Groundwater <b>D</b> Chemical Data	Perchlorate Isotope Results	Conclusion
MW-16	0	0		$\Diamond$	Δ	JPL Source
MW-17-3	3,000	0		$\Diamond$	Δ	JPL Source
LAWC#3	3,500	0		$\Diamond$	Δ	JPL Source
LFWC#2	7,800	•		<b>♦</b>		Non-JPL Source
Bangham Well	15,500	•		<b>*</b>		Non-JPL Source
Sunset Well	16,000	•		<b>*</b>		Non-JPL Source
Garfield Well	21,000	•		<b>*</b>		Non-JPL Source
MW-19-2	4,000	•		•		Non-JPL Source
MW-25	15,000	•		<b>*</b>		Non-JPL Source
MW-21	3,000			•	NA	Non-JPL Source

JPL Source

#### Non-JPL Source

- Type 3 or more direct mixing with Colorado River Water, sulfate
- Not located in the flow path of chemicals originating from JPL on JPL and RBMB Groundwater Models.
- ◆ No carbon tetrachloride (JPL tracer) detected in groundwater samples.
- ▲ Perchlorate isotope fingerprint indicates non-JPL source(s).

Figure R6. Any conceptual site model proposed for understanding the extent of JPL perchlorate needs to be corroborated by all available data and be applicable in cases where JPL perchlorate is a source and where it is not. Our proposed conceptual site model meets these criteria, confirming NASA's perchlorate in MW-16, MW-17-3, and LAWC#3, and providing a compelling argument that NASA's perchlorate is not associated with the Sunset Reservoir wells.

O Type 1 Water

<sup>□</sup> Located downgradient and within the flow path of chemicals originating from JPL based on JPL and RBMB Groundwater Models.

Co-located carbon tetrachloride (JPL tracer) and perchlorate in groundwater samples.

 $<sup>\</sup>stackrel{\cdot}{\triangle}$  Perchlorate isotopic fingerprint consistent with JPL source

#### ATTACHMENT NO. 1: RESPONSES TO COMMENTS FROM THE EPA

On January 31, 2007, the National Aeronautics and Space Administration (NASA) released a study¹ regarding the extent of perchlorate and other chemicals in groundwater originating from the Jet Propulsion Laboratory (JPL) site. The objectives of the study were to (1) evaluate the downgradient (southern) extent of chemicals originating from the JPL facility and (2) determine if the occurrence of perchlorate in the Sunset Reservoir area was associated with migration from the JPL facility. The U.S. Environmental Protection Agency (EPA) reviewed the NASA report and submitted comments. Responses to EPA's comments are provided below.

#### **GROUNDWATER MODELING**

**EPA Comment No. 1 -** The TM/AIR does not specifically discuss why the results of this groundwater modeling effort differ from information presented in the *Final Operable Unit 3 Remedial Investigation RI Addendum Work Plan*, Battelle 2004 (OU 3 RI Addendum WP). The OU 3 RI Addendum WP indicates that the Coupled Flow and Energy Solute Transport model was used to simulate groundwater flow in the Raymond Basin and the potential groundwater migration pathways and particle tracking from near the Arroyo Seco Spreading Grounds was performed for the period from 1989 to 2023. The simulation results found a flow path from the Arroyo Seco Spreading Basin and the unsewered La Cañada-Flintridge area towards the City of Pasadena production wells located near the Sunset reservoir. However, the TM/AIR states that particle tracking indicates that groundwater originating to the west of JPL in La Cañada-Flintridge flows south of the JPL facility and then heads towards the Sunset Reservoir wells. It is unclear why these two model results would differ and the TM/AIR does not provide an explanation. Please explain why these two models differ in their results.

## NASA's Response:

The Coupled Flow and Energy Solute Transport (CFEST) model, JPL Model, and RBMB Model are all in agreement on groundwater flow paths. Although the basin-scale CFEST model<sup>2</sup> and the JPL Model that were referenced in the Remedial Investigation (RI) Addendum Work Plan<sup>3</sup> were designed with different purposes, they are consistent in their representation of the groundwater flow fields in the Monk Hill Subarea. The particle tracking performed using the CFEST model evaluated particle releases from the La Cañada Flintridge area (cross-gradient and west of JPL) and from the southern end of the Arroyo Seco spreading grounds (south of the JPL facility and the City of Pasadena production wells). *The particle tracking simulations performed using the CFEST model did not evaluate a release from the JPL facility.* Results of particle tracking simulations performed using the JPL Model and the RBMB Model support the results of the CFEST model, in that groundwater to the west of JPL and from the southern end of the Arroyo Seco spreading grounds (south of the City of Pasadena production wells) will migrate to the Sunset Reservoir wells. Groundwater modeling performed using the JPL Model indicates that dissolved chemicals originating from the JPL facility would be contained by production wells in the Monk Hill Subarea.

**EPA Comment No. 2 –** As a general observation, it is unclear from the TM/AIR whether the model has been applied in a way that is specific enough to address the objective of an almost absolute capture of perchlorate originating from the JPL site. The objective(s) and the assumptions of the model used to predict

<sup>&</sup>lt;sup>1</sup> NASA. 2007. *Technical Memorandum: Additional Investigation Results*. Prepared by Battelle for the National Aeronautics and Space Administration. January.

<sup>&</sup>lt;sup>2</sup> CH2M-Hill. 1992. First Technical Assessment, Phase 2 Report, Devil's Gate Multi-Use Project. Prepared by CH2M-Hill for the City of Pasadena Water and Power Department. July.

<sup>&</sup>lt;sup>3</sup> NASA. 2004. *Operable Unit 3 Remedial Investigation (RI) Addendum Work Plan (Pasadena Sampling Plan [PSP]-2004-1).* Prepared by Battelle for the National Aeronautics and Space Administration. November.

capture are not described. For example, if the model objective and assumptions were to predict the capture zone of future pumping, it is inappropriate to make conclusions about the past capture zones of the same wells, especially if the pumping history of the wells is different. Please describe the model objective(s) and model assumptions regarding the pumping history, scale of the model, and the geohydrologic and other features supporting that an adequate capture zone analysis has been conducted.

## NASA's Response:

A detailed discussion on the construction and calibration of the JPL Monk Hill steady-state groundwater model is presented in the JPL Groundwater Modeling Report.<sup>4</sup> In the interest of length, only a brief discussion of the model was presented in the Additional Investigation Technical Memorandum.<sup>1</sup> The overall objective of the groundwater modeling effort was to evaluate the potential fate and transport issues related to chemicals in groundwater and to develop site remediation strategies for both on-facility and off-facility groundwater. The application of the JPL Model for the Additional Investigation is consistent with this objective. The modeling effort was evaluated with respect to the guidelines established in the recent EPA guidance document associated with evaluating capture zones.<sup>5</sup> Table A1-1 shows that a thorough evaluation was performed to ensure that the model was applied correctly with respect to capture zones.

**EPA Comment No. 3 –** The RBMB model is a two layer regional model, and the JPL model is a more localized site model consisting of four layers. Figures 2, 3, and 4 show particle tracking simulation results. Considering the existence of the vertical hydraulic gradient, the particle paths would look different for each layer. The composite paths shown in Figures 2, 3, and 4 are then not sufficient to describe the three-dimensional nature of the particle paths. Please show the information for each layer rather than as a composite. Please show the particle paths in cross-section as well as forward paths originating at JPL.

#### **NASA's Response:**

As requested, Figures A1-1, A1-2, A1-3, and A1-4 have been prepared to show capture zones in each of the four zones defined in the JPL Modeling Report. A lithologic cross section representing a transect from the JPL source area to the downgradient production wells is shown in Figure A1-5. These figures show that the production wells provide vertical and horizontal containment of chemicals originating from JPL.

**EPA Comment No. 4 –** A closer view of Figures 3 and 4 does not support the TM/AIR conclusion that the flow fields of the RBMB and JPL Models are "very similar." Considering the size of the grids, the number of layers, etc., it is not surprising that the results of the two models would be different. It is important to realize that we are not looking at the whole model domain, but rather a small (JPL) area within the large model domain. Please elaborate on how the two models can be regarded as similar when the grid sizes and layers are different.

## NASA's Response:

Although the basin-scale RBMB Model and the subarea-scale JPL Model were designed with a different purpose in mind, they are consistent in their representation of the overall groundwater flow field in the vicinity of the JPL facility. Specifically, both models indicate that the capture zones of the Monk Hill Subarea extraction wells encompass the JPL facility. Because of the finer descritization and focus on the Monk Hill Subarea, the flow field predicted using the JPL Model is more accurate than the RBMB model in the vicinity of JPL.

<sup>&</sup>lt;sup>4</sup> NASA. 2003. *JPL Groundwater Modeling Report*. December.

<sup>&</sup>lt;sup>5</sup> U.S. EPA. 2008. A Systematic Approach to the Evaluation of Capture Zones at Pump and Treat Systems. EPA 600/R-08/003. Office of Research and Development. National Risk Management Research Laboratory. January.

Table A1-1. A thorough evaluation was conducted as part of the JPL Model capture zone analysis based on EPA guidance.

EPA Step <sup>5</sup>	EPA Guidance Suggestions <sup>5</sup>	JPL Model Plume Capture Zone Evaluation
1. Data review	<ul> <li>Review and compile site data</li> <li>Prepare a conceptual site model (CSM)</li> <li>Understand remedy objectives</li> </ul>	<ul> <li>Reviewed and documented previous groundwater modeling efforts</li> <li>Prepared detailed CSM that is documented in the JPL modeling report</li> <li>Network of 26 shallow and multi-port monitoring wells installed in study area</li> <li>Quarterly chemical and groundwater level monitoring data compiled in site database</li> <li>Performed large scale aquifer test using remedial action wells and existing site monitoring wells (4 multi-port wells and 5 shallow wells)</li> <li>3-D numerical groundwater flow model prepared for Monk Hill Subarea</li> <li>Specific groundwater modeling objectives outlined in the JPL modeling report</li> </ul>
2. Define site-specific target capture zone(s)	<ul> <li>Evaluate in 3D</li> <li>Target capture zone should be clearly stated in remedial action and monitoring plans</li> <li>Should consider each contaminant</li> <li>Should be defined in terms of specific criteria</li> </ul>	<ul> <li>3-D lithologic block diagram prepared for the Monk Hill subarea using available lithologic information from existing monitoring wells and municipal production wells</li> <li>3-D numerical groundwater flow model prepared for Monk Hill Subarea</li> <li>Plume maps prepared showing extent (maximum contaminant level [MCL] or Action Level) of individual chemicals</li> </ul>
3. Interpret groundwater levels	<ul> <li>Prepare potentiometric surface maps (horizontal) and groundwater level difference maps (vertical)</li> <li>Evaluate flow directions using groundwater level pairs (gradient control points)</li> </ul>	<ul> <li>Historical groundwater flow patterns in the vicinity of the site are well understood</li> <li>Potentiometric surface maps prepared for each quarterly monitoring event</li> <li>Multi-port monitoring wells (5 zones in each well) allow for evaluation of vertical flow</li> <li>Flow directions evaluated using groundwater level data from well pairs throughout the site</li> <li>Groundwater flow model developed and calibrated to groundwater levels measured in 26 shallow and multi-port monitoring wells and municipal production wells in the study area</li> </ul>
4. Perform calculations	<ul> <li>Estimated flow rate calculations</li> <li>Capture zone width calculations (can include drawdown calculation)</li> <li>Groundwater modeling (analytical or numerical) to simulate water levels, in conjunction with particle tracking and/or transport modeling</li> </ul>	<ul> <li>Flow directions and rates evaluated using simple analytical calculations with groundwater level data from well pairs throughout the site</li> <li>Previous groundwater modeling efforts evaluated flow direction and rates in the Basin</li> <li>3-D steady-state numerical groundwater flow model prepared for Monk Hill Subarea</li> <li>JPL Model is consistent with previous groundwater models developed for the Monk Hill Subarea and the Raymond Basin (i.e., CFEST Model).</li> <li>Independently developed groundwater flow model developed by RBMB supports flow patterns in the vicinity of the Monk Hill Subarea and JPL.</li> <li>Extensive forward and backward particle tracking simulations performed with JPL model to evaluate flow paths from the JPL facility and capture zones of existing municipal production wells</li> </ul>

EPA Step <sup>5</sup>	EPA Guidance Suggestions <sup>5</sup>	JPL Model Plume Capture Zone Evaluation
		<ul> <li>Particle tracking shows particle flow paths released from the source area mimic known distribution of carbon tetrachloride</li> <li>Varying historical and proposed extraction rates have been used to evaluate production well capture zones from different remedial alternatives</li> <li>Although model is steady state, results from transient flow calibrations indicate the model is appropriate for evaluating conditions at the site</li> <li>Analytical models used to back-calculate chemical concentrations from extraction wells to source area to evaluate attenuation rates</li> <li>Transient simulations performed to evaluate the effects of seasonal pumping schedules on groundwater flow paths and production well capture zones</li> </ul>
5. Evaluate concentration trends	Monitor downgradient concentration trends to interpret capture	<ul> <li>Network of 26 shallow and multi-port monitoring wells installed in study area; several of these wells are downgradient of the leading edge of plume migration</li> <li>Downgradient municipal production wells monitored for chemical concentrations;</li> <li>Chemical concentrations in downgradient well MW-20 indicate the plume from JPL is contained by the extraction wells; sporadic detections in deep screens in this well likely correlate to a period when the extraction wells were offline (1985-1990)</li> <li>Carbon tetrachloride data support that the leading edge of the plume is established</li> <li>Isotope analysis performed to evaluate signature of chemicals released at the site and differentiate between different sources within the study area</li> </ul>
6. Interpret capture	<ul> <li>Interpret actual capture based on Steps 1-5.</li> <li>Compare actual capture to target capture zone.</li> <li>Assess uncertainties and data gaps</li> <li>Evaluate need to increase/reduce extraction rates</li> </ul>	<ul> <li>Particle tracking simulations indicate chemicals originating from JPL will be contained by existing municipal production wells</li> <li>Production well capture zones indicate groundwater in the vicinity of JPL will be contained</li> <li>Varying historical and proposed extraction rates have been used to evaluate production well capture zones from different remedial alternatives</li> </ul>

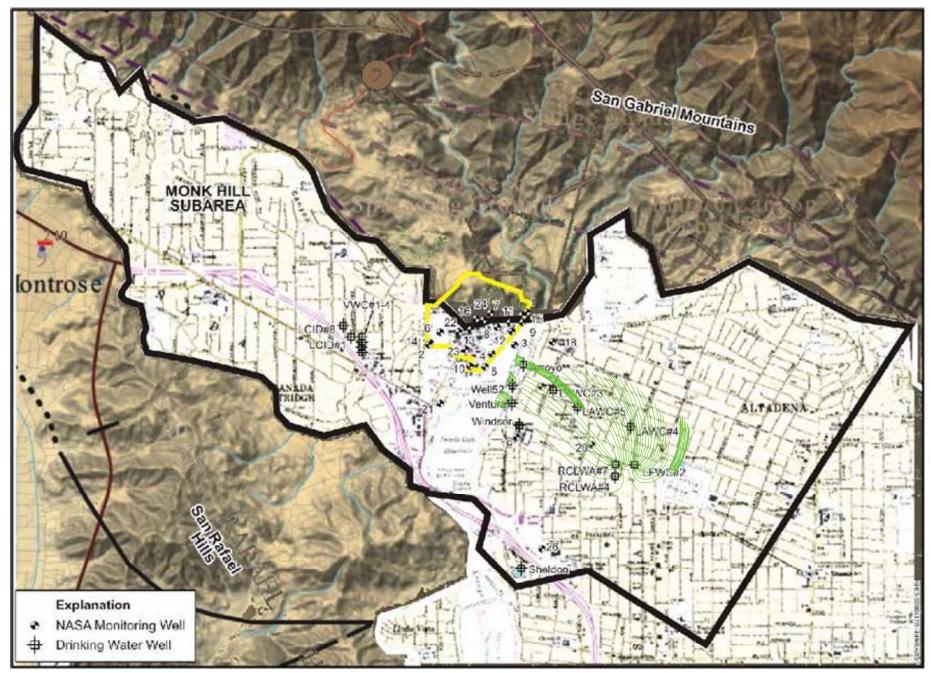


Figure A1-1. Capture zones in JPL Model Layer 1 - backward particle tracking from Monk Hill Subarea production wells.

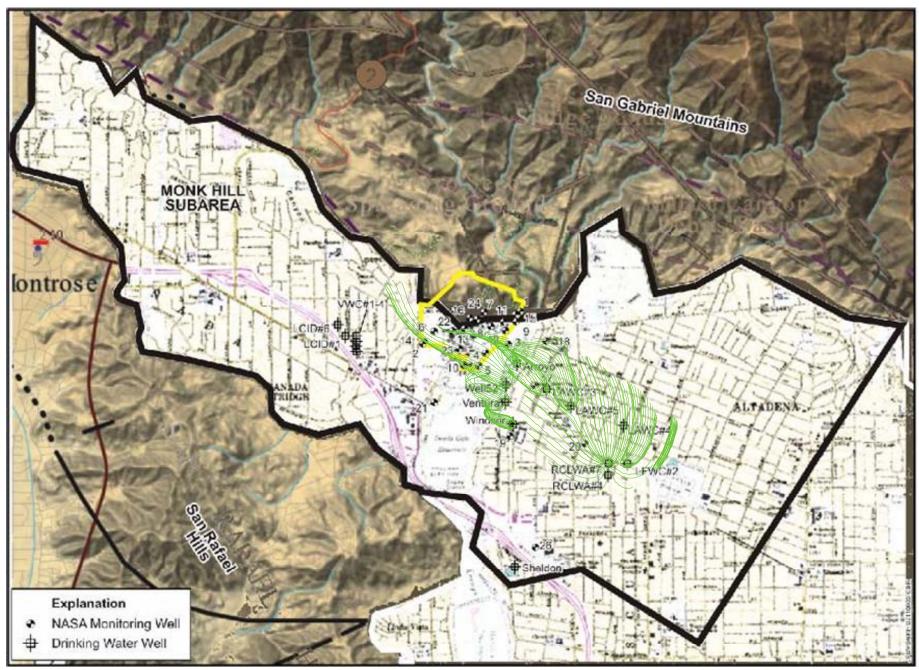


Figure A1-2. Capture zones in JPL Model Layer 2 - backward particle tracking from Monk Hill Subarea production wells.

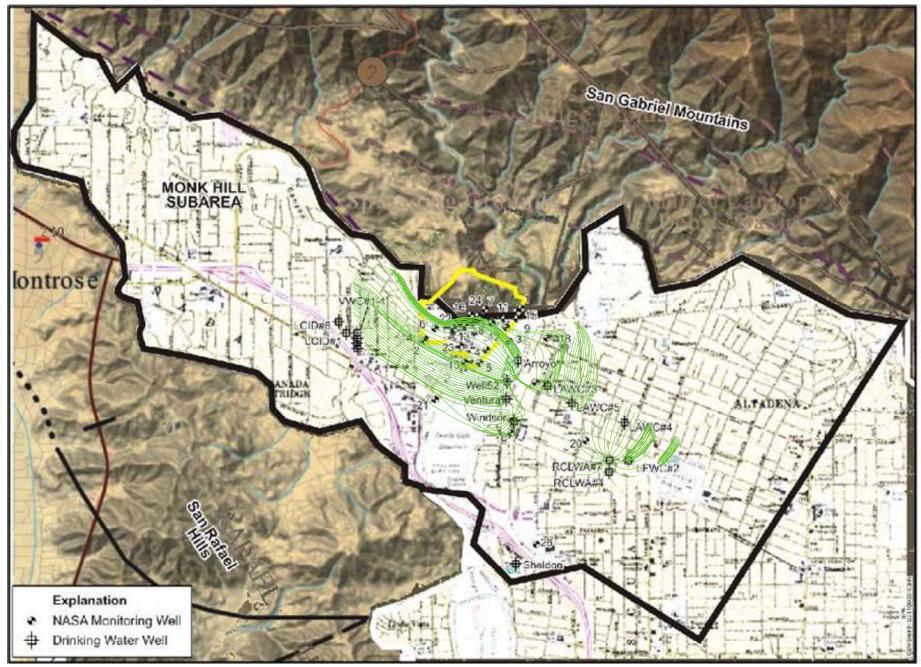


Figure A1-3. Capture zones in JPL Model Layer 3 - backward particle tracking from Monk Hill Subarea production wells.

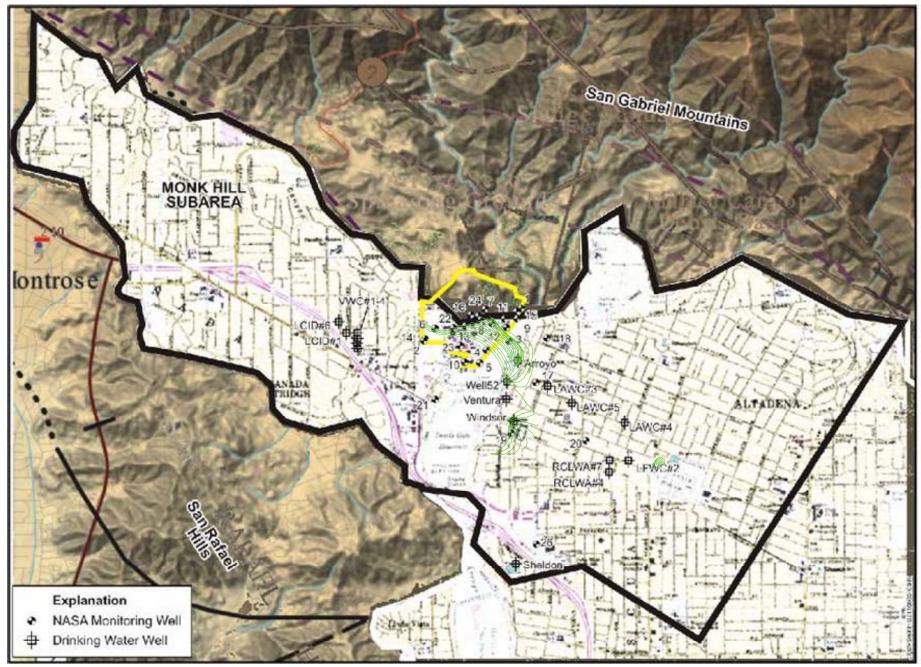


Figure A1-4. Capture zones in JPL Model Layer 4 - backward particle tracking from Monk Hill Subarea production wells.

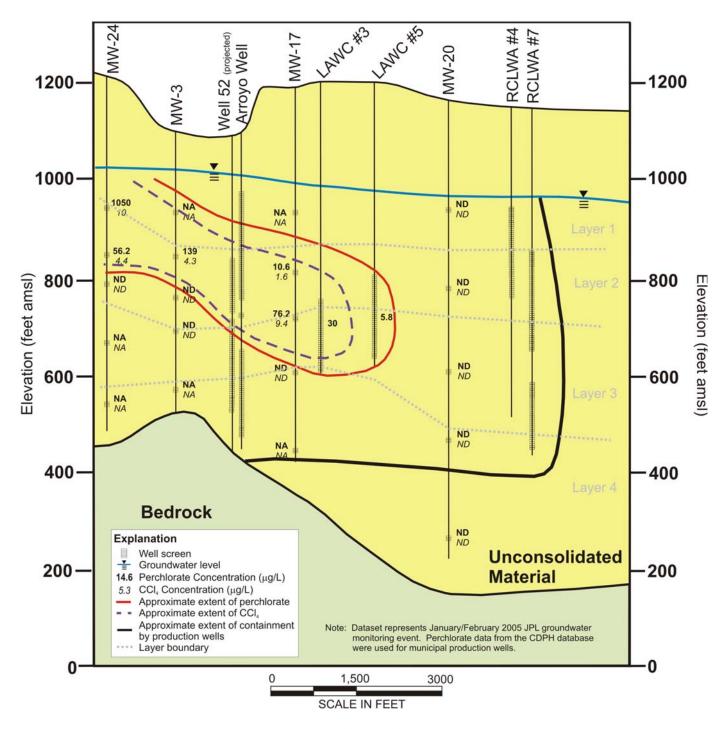


Figure A1-5. This cross-section shows the location of the different layers in the JPL Model, the extent of carbon tetrachloride and perchlorate prior to initiation of the source area treatment system, and the approximate extent of containment by Monk Hill Subarea production wells.

**EPA Comment No. 5 -** The JPL model uses the average extraction rates observed between 1960 and 2000. The production wells "Arroyo Well" and "Well 52" are listed as the most important wells. However, these two wells were not operating for five years (1985-1990). It is not clear whether there are other periods when the wells were not operational, but the five-year period was mentioned as the "longest period" when the wells (and two other wells) were not pumping. Please also explain the basis for the statement that "... the chemicals would have been drawn back upon reinitiating operation of these wells..." (Page 11, first paragraph). Each production well has a stagnation point downgradient from the well. If the well is shut down for some duration and the contaminant passes the stagnation point, restarting the well (assuming the same pumping rate and the same regional flow) will not recapture the escaped contaminant.

## NASA's Response:

The period from 1985 to 1990 was the longest period during which there was very little production from the Arroyo Well, Well 52, LAWC#3, and LAWC#5. Historical pumping records indicate that there are no other significant periods since 1960 that these wells were not operational (see Figure R1 in the general response). Sporadic detections of perchlorate in MW-20 from 1998 through 2003 are believed to be associated with the shutdown from 1985 to 1990 based on our understanding of groundwater flow paths and estimated travel times. As stated in the technical memorandum, much of the chemicals would have been drawn back upon reinitiating operation of these wells based on their location and projected capture zones, and the remaining chemicals would likely have been captured by other production wells in the Monk Hill Subarea (Ventura Well, Windsor Well, RCLWA#4, and RCLWA#7) that were active at this time. Transient simulations performed using the JPL Model, and documented in the JPL Modeling Report,<sup>4</sup> to evaluate the effects of seasonal pumping schedules on groundwater flow paths and production well capture zones indicated containment was not compromised. In addition, even if groundwater had bypassed the Monk Hill Subarea production wells during this time period, based on estimated migration rates it could not yet have reached the Sunset Reservoir wells.

**EPA Comment No. 6 –** The TM/AIR does not adequately discuss the perchlorate detections in MW-25 in the context of why these additional monitoring wells were proposed in the OU 3 RI Addendum Work Plan. The OU 3 RI Addendum WP proposed installing MW-25 and MW-26 to verify the location of the leading edge of the JPL perchlorate plume and discusses that these monitoring wells were specifically located between MW-20 and the Sunset Reservoir wells to verify that the leading edge of the plume had traveled beyond the MW-20 location. Subsequently, the purpose of the TM/AIR appears to have changed from specifically verifying the location of the leading edge of the plume to a discussion of other perchlorate sources. Please discuss if the leading edge of the perchlorate plume was established.

#### NASA's Response:

The Additional Investigation Technical Memorandum¹ defined the southern extent of the perchlorate plume by stating that the plume was contained in the Monk Hill Subarea. We now understand that this could be confusing. Monitoring data collected from MW-19, MW-21, MW-20, and MW-26 define the leading edge of JPL perchlorate plume. Sporadic detections of perchlorate in MW-20 in 1998, 2002, 2003, and 2008 represent the furthest migration of perchlorate originating from JPL. MW-20 is within the capture zone of RCLWA wells. MW-25 is located near the Sunset Reservoir wells and perchlorate detections in samples collected from MW-25 are not associated with JPL.

**EPA Comment No. 7 -** The TM/AIR does not discuss the potential impact of the top of bedrock and its relationship to the perchlorate detections in MW-25 as well as the Sunset Reservoir wells. Perchlorate is detected at depth at the MW-25 location consistent with depths to bedrock in MW-19. Please provide a discussion of the potential for perchlorate to enter bedrock and migrate toward the Sunset Reservoir wells.

Due to the significantly lower permeability of the bedrock compared to the overlying unconsolidated material, the potential for chemical migration into the bedrock is minimal and unlikely. Hydraulic conductivity estimates for the type of bedrock encountered beneath the Monk Hill Subarea range between three and four orders of magnitude lower than the overlying unconsolidated material at the site. In addition, historical data from the deepest screen of the multi-port JPL monitoring well MW-19 show perchlorate concentrations consistently below 5  $\mu$ g/L since 1997.

**EPA Comment No. 8 –** The assumption that groundwater contamination is contained by wells in the Monk Hill Subarea appears to be based on recent and current groundwater extraction rates and information other than historical conditions. In addition, although the text indicates that there were no periods "since the early 1940s of sustained shutdown of all of these Monk Hill Subarea wells," shutdown or intermittent operation of one or more wells may have allowed migration of perchlorate beyond the Monk Hill Subarea. In addition, it is likely that these water supply wells extracted water from the deeper portions of the aquifer, so perchlorate contamination may have migrated in the shallower layers. Further, historical pumping rates may have been less than current pumping rates; Table 2-1 of the OU 3 RI Addendum WP³ indicates that the maximum extraction rate in several of the wells occurred in the 1960s, 1990s, or 2000. Since many of the wells apparently pumped at lower rates in the 1940s and 1950s, it is likely that "containment" of the perchlorate plume was not achieved. Statements about containment of the perchlorate plume should either be deleted from the text or modified to specify the period of years to which the conclusions applies. In addition, historical low extraction rates could be used in the model to evaluate the potential that perchlorate migrated beyond the Monk Hill Subarea.

## NASA's Response:

Particle tracking simulations have been performed using several pumping scenarios, each of which shows containment of particles released from JPL. The simulations presented in the JPL Modeling Report uses an average pumping rate from 1996-2000, whereas the simulations presented in the Additional Investigation Technical Memorandum<sup>1</sup> used an average pumping rate for the period between 1960 and 2000. Figure R1 in the general response shows consistent annual pumping from Monk Hill Area production wells between 1960 and 2000. This timeframe is believed to be appropriate given our understanding of when the chemicals were released and projected travel times. Perchlorate used during testing at JPL in the mid-1940s and 1950s would have traveled from seepage pits through almost 200 feet of vadose zone and then in groundwater approximately 2,500 feet to the closest production well, the Arroyo Well. Conservative estimates indicate vadose zone travel times of at least 7.5 years and travel times in groundwater of at least 11 years. Therefore, considering extraction rates between 1960 and 2000 provides an appropriate evaluation timeframe. In addition, transient simulations performed using the JPL model to evaluate the effects of seasonal pumping schedules on groundwater flow paths and production well capture zones indicated containment was not compromised. Production wells in the Monk Hill Subarea are screened in the shallow and deep portions of the aquifer (see Figure A1-5) and an evaluation of cross-section and plan view particle tracking maps indicate containment of shallow and deep groundwater in the vicinity of JPL.

**EPA Comment No. 9 -** There are only a few wells in the area between JPL and the Sunset Reservoir Area, so this area cannot be considered well characterized and the potential for preferential migration pathways should be considered. Preferential migration pathways or channels are common in the depositional environments that resulted in the subsurface lithology between JPL and the Sunset Reservoir Area. These preferential migration pathways may have facilitated perchlorate migration to the Sunset Reservoir Area. The text should be revised to acknowledge this possibility.

It is agreed that preferential flow paths may exist within the Raymond Basin. Evaluation of the bedrock elevation, the groundwater flow field, and the particle tracking simulations of the RBMB Model confirm the presence of a north-south preferential flow path between Monk Hill and the San Rafael Hills that funnels groundwater from the west and south of JPL toward the Sunset Reservoir wells. Because of operation of the Monk Hill production wells (and the resulting size of the well-specific capture zones), preferential flow near the JPL facility would be channeled toward the Monk Hill Subarea production wells and contained.

**EPA Comment No. 10 -** The following statements in the TM/AIR are of concern for the accuracy of the results of the model, and should be addressed in future modeling efforts.

- Page 6, paragraph 2: "... vertical hydraulic head differences with depth are observed... this indicates that the aquifer does not exhibit truly unconfined conditions..." Please recognize that the existence of the vertical hydraulic gradient alone does not indicate whether the aquifer is confined or unconfined.
- Page 6, paragraph 5: "...groundwater elevations have fluctuated up to 75 ft each year beneath JPL..." Such large water table fluctuations indicate strong transient conditions at the site. Any steady-state model that represents some "average conditions" in the future would be less reliable because of the fluctuations.
- Page 7, paragraph 1: "...as part of the steady-state model development, a transient model was constructed using data from 1996-2000." If the water levels at the Site fluctuated up to 75 ft, it needs to be clarifies how the transient model calibration is similar to the steady-state model calibration.

## NASA's Response:

It is agreed that the existence of vertical gradients alone does not indicate whether an aquifer is confined or unconfined. Several factors were evaluated to determine aquifer conditions in the Basin, including the effects of pumping, the lithology (individual silt beds), and vertical anisotropy. It also is agreed that the observed groundwater fluctuations are indicative of transient conditions, and that care should be taken when using the steady-state model to predict future conditions. Results from a transient modeling performed during development of the JPL Model indicated that the calibrated flow field in the steady-state groundwater flow model (that averaged input parameters over a four year period) was similar to that generated under transient conditions. This similarity indicates that the steady state model can be effectively used to perform simulations designed to meet the modeling objective of evaluating fate and transport issues and developing site remediation strategies.

#### **GROUNDWATER GEOCHEMISTRY**

**EPA Comment No. 1 –** This section provides a thorough discussion of the groundwater types, water imports, likely anthropogenic sources of constituents – including perchlorate – to groundwater, and an interpretation of how the general water quality has been impacted by such sources. While the section does not present information suggesting the significant amounts of perchlorate in imported water were introduced into the Raymond basin by the Metropolitan Water District (MWD) distribution system, there is no information that assists in evaluating the respective contribution of perchlorate from various sources (MWD, JPL, fertilizer applications, etc.).

Data on the contributions of perchlorate from various sources do not exist. All available data were evaluated together to obtain the best possible understanding of the extent of JPL chemicals and whether or not perchlorate originating from JPL may be the source of perchlorate in the Sunset Reservoir wells. Groundwater modeling indicated that groundwater originating from JPL would be contained by wells in the Monk Hill Subarea and not migrate to the Sunset Reservoir area. Carbon tetrachloride and perchlorate data indicate that the southern extent of JPL perchlorate is defined and does not extend beyond the Monk Hill Subarea. Carbon tetrachloride data also corroborate the groundwater modeling results. Groundwater geochemistry and perchlorate isotope data demonstrate that other sources of perchlorate exist in the Basin. Taken together, the data support that the extent of perchlorate originating from JPL is contained within the Monk Hill Subarea, with MW-20 representing the southeastern extent of the plume. Thus, the data provide a compelling picture that perchlorate originating from JPL has not reached the Sunset Reservoir wells.

#### GROUNDWATER CHEMICAL CONCENTRATION DATA

**EPA Comment No. 1 -** The analysis that carbon tetrachloride is a reliable tracer for perchlorate originating from JPL is not a valid assumption for several reasons. One reason is that monitoring data indicate that the groundwater concentrations of perchlorate are typically higher than the carbon tetrachloride concentrations, and therefore simple dilution due only to advective flow and dispersion should result in carbon tetrachloride reaching non-detectable concentrations before perchlorate would similarly become non-detect.

## NASA's Response:

NASA recognizes the effect of advective and dispersive flow on contaminant concentrations, particularly in the absence of hydraulic containment. As such, the historic movement of the carbon tetrachloride through the Monk Hill Subarea has helped further our understanding of the JPL perchlorate plume by identifying areas that are hydraulically connected. While carbon tetrachloride concentrations are lower than perchlorate concentrations by a factor of approximately 10, the detection limit for carbon tetrachloride is also lower than perchlorate by a factor of approximately 10. Therefore, the use of carbon tetrachloride as a tracer is not limited by the relative concentrations between it and perchlorate. In addition, we see a strong correlation between perchlorate and carbon tetrachloride in LAWC#5, located approximately 1 mile from the JPL source area (see Figure R4 in the general response). Therefore, NASA continues to believe that the use of carbon tetrachloride as a tracer is appropriate as one line of evidence to help understand the extent of JPL perchlorate.

**EPA Comment No. 2 –** The use of carbon tetrachloride (an organic compound) as a reliable tracer is also difficult to support because it can undergo transformation reactions whereas perchlorate (an inorganic ion) is more stable. As a measure of the ease of reduction of carbon tetrachloride, its reduction/oxidation half-reaction potential is relatively high, between that of denitrification (nitrate reduction to nitrogen) and reduction of tetrachlorethene (PCE to trichloroethene). Furthermore, the environmental literature has several citations to transformations of carbon tetrachloride by microbial processes and chemical processes (abiotic reactions); the later processes are a result of residual effects of microbial processes that create chemical conditions (mineral surfaces, sulfides) where carbon tetrachloride is subsequently transformed (reduction reactions). In the expected predominate aerobic subsurface it is expected that such reducing conditions will be present but sporadic, and probably due to localized leaching of constituents with infiltrating surface waters (maintenance, landscaping, irrigation, etc.); the sporadic presence and very low concentrations of such reactant systems and possible transformation products obviously makes the identifications of such adventitious processes almost impossible.

NASA agrees with the EPA's description of the aquifer oxidation-reduction (redox) conditions and the potential, albeit small, for carbon tetrachloride to undergo transformation reactions. The available data overwhelmingly support aerobic conditions in the aquifer near JPL and do not indicate that reducing conditions exist, which would impact the carbon tetrachloride and perchlorate plumes originating from JPL (see general response). Therefore, NASA believes the aquifer redox conditions support the use of carbon tetrachloride as a tracer.

**EPA Comment No. 3 -** In summary, it is plausible to qualitatively consider carbon tetrachloride as a tracer for perchlorate originating from the JPL site as long as both constituents are detected in the groundwater sampling program, but the absence of carbon tetrachloride in a groundwater sample cannot be the basis for the conclusion that perchlorate in the sample is not from the JPL site.

## NASA's Response:

NASA appreciates the EPA's understanding of the unique site conditions at JPL, which recognize the applicability of carbon tetrachloride as a tracer, understanding that perchlorate could travel more rapidly in groundwater in the absence of containment. As such, NASA would like to restate that our approach to evaluate the downgradient extent of chemicals and the origin of perchlorate in the Sunset Reservoir area is based on an integrated evaluation of all available data. This evaluation supports that the extent of perchlorate originating from JPL is contained within the Monk Hill Subarea, with MW-20 representing the southeastern extent of the plume.

#### PERCHLORATE ISOTOPE DATA

**EPA Comment No. 1 -** The conclusion that the isotopic signature of perchlorate samples collected from the downgradient wells is different from the signature of perchlorate at the JPL site and therefore that JPL is not a source of perchlorate does not adequately take into consideration that the measurements on the downgradient water samples are possibly a composite from several sources of perchlorate to the Raymond basin. The TM/AIR does make a persuasive case that several sources are reasonably suspect, and that there may be other sources of perchlorate that cannot be identified. The complexity of the multiple sources, as well as the unknown contribution of these sources, does not eliminate JPL as one possible contributor of perchlorate to the downgradient wells based on the isotopic data alone.

Review of the perchlorate isotope data indicate several uncertainties that confound an interpretation of the data that could be applied in source allocation. As discussed in the TM/AIR,¹ the most reasonable suspected sources of perchlorate to the downgradient wells are the JPL facility, Colorado River water, and fertilizer perchlorate (dark blue diamond in yellow shaded area, light blue circles, and orange squares, respectively, on Figures 16 and 17). However, there is significant scatter of the isotopic signatures of samples from each suspected source which has been attributed to different batches of the source perchlorate. Additionally, the perchlorate samples from the multi-level well MW-25 show no clear trends that can be interpreted as hydrostratiographic ones that have been impacted by discrete sources. For example, the isotopic signature of the shallowest sample (MW25-1) most closely resembles the JPL source perchlorate, which would be expected to be at greater depths from a further upgradient source. Additionally, the isotopic signatures of the samples from the intermediate depths, MW25-2 and MW25-3, appear to resemble the Colorado River water samples in the <sup>37</sup>Cl/¹8O plot (Figure 16), but the same two samples are the most anomalous in the <sup>17</sup>O/¹8O plot.

While the perchlorate isotope data do not support a conclusion, the source of the perchlorate in the downgradient wells is solely due to JPL. The data also do not eliminate JPL as a contributing source of perchlorate to the downgradient wells in an obviously complex geohydrologic system with several possible sources of perchlorate.

## NASA's Response:

To restate EPA's comment, the perchlorate isotope data present a good case for multiple sources of perchlorate, but they do not rule out JPL as a possible contributor. NASA would like to stress again the importance of using all available data to understand the extent of JPL perchlorate. Specifically, the isotope data must be considered in the context of the groundwater monitoring data, geochemical data, and the groundwater modeling results. When this is done, we believe the data provide a compelling picture that perchlorate originating from JPL has not reached the Sunset Reservoir wells.

In addition, NASA's conclusion that Sunset Well does not contain JPL perchlorate is supported by isotope data from MW-19 (Screen 2), which is isotopically indistinguishable from that from the Sunset Well. Since MW-19 is a JPL monitoring well, we know much about this well, including that the source of perchlorate in MW-19 (Screen 2) did not originate from JPL. This is supported by the fact that carbon tetrachloride has never been detected in MW-19 (Screen 2) even though it is less than a mile from JPL. This is because MW-19 is cross-gradient from JPL (i.e., not within the flow path of a particle originating from JPL). In addition, tritium data indicate recently recharged water at this well location, which is consistent with injection of imported water upgradient of MW-19 in the Valley Water Company wells. Also, groundwater modeling indicates that groundwater from cross-gradient and to the west of JPL flows past MW-19 and on toward the Sunset Reservoir wells. Therefore, MW-19 (Screen 2) and the Sunset Well may contain perchlorate from the same source, but not from JPL.

The comment that MW25-2 and MW25-3 samples look most like Colorado River perchlorate (i.e., Las Vegas Wash) is noteworthy. Furthermore, when the MW25-2 and MW25-3 samples are considered in conjunction with Figure 5 (O-17 plot) where those samples are most "anomalous", EPA's comment suggests that the Colorado River perchlorate also contains some appreciable amount of agricultural perchlorate. Most importantly, the same could apply to Garfield and Bangham samples. In summary, when the isotope data are considered within the context of the geochemical data and the hydrologic constraints, the lines of evidence show that some fraction of the perchlorate found in MW-25, as well as the Garfield and Bangham samples, originated from natural/agricultural sources.

#### ATTACHMENT NO. 2: RESPONSES TO COMMENTS FROM THE DTSC

On January 31, 2007, the National Aeronautics and Space Administration (NASA) released a study¹ regarding the extent of perchlorate and other chemicals in groundwater originating from the Jet Propulsion Laboratory (JPL) site. The objectives of the study were to (1) evaluate the downgradient (southern) extent of chemicals originating from the JPL facility and (2) determine if the occurrence of perchlorate in the Sunset Reservoir area was associated with migration from the JPL facility. The California Department of Toxic Substances Control (DTSC) reviewed the NASA report and submitted comments. Responses to DTSC's comments are provided below.

DTSC Comment No. 1 - Page 6. Background. The background lacks a description of the depositional environment of the alluvium of the Monk Hill basin. The depositional environment determines large-scale features of the groundwater system that may affect contaminant migration. Most of the alluvium near JPL was deposited by the Arroyo Seco, which is one of the largest local drainages. The landform is an alluvial fan, characterized by about 10% coarse channel deposits and 90% flood overbank deposits, which may develop flat soil horizons. The stream channels have permeability contrast with the material they incise, and this stream fabric imparts a strong lateral anisotropy to groundwater flow. Other features of the alluvium include detrital charcoal, which is deposited after brushfires. This naturally occurring carbon also affects contaminant transport. The section should include a discussion of the geological factors that affect groundwater flow.

## NASA's Response:

The depositional environment of the Monk Hill Basin is well documented<sup>2,3</sup> including the anisotropy associated with the alluvium. While lateral anisotropy, resulting in preferential pathways, likely exists at a small scale near JPL due to the depositional environment in the Raymond Basin, these pathways do not impact our understanding of groundwater flow at the scale of our study (i.e., Sunset Reservoir wells are over three miles from JPL). Data collected during the Remedial Investigation (RI), the JPL modeling effort, and the RBMB modeling effort indicate that groundwater flow is primarily controlled by the bedrock surface and pumping, not the current location of the Arroyo Seco stream bed, which is over 100 feet above the groundwater table in the Monk Hill Subarea. See response to General Comment No. 1.

Upon reviewing all available boring logs for monitoring wells (MW-1 through MW-26), soil borings (B-1 through B-19, B-20, B-20A, B-21 through B-23, B-23A, B-23B, B-24, and B-25 through B-39 [Sonic]), extraction wells (EW-1, EW-2, and EW-3), injection wells (i.e. IW-1, IW-2, and IW-3), municipal production wells (Arroyo, Well 52, Ventura, and Windsor), dewatering wells (Well # 15 – 17), and JPL Thrust Fault investigation boring logs and trench logs, detrital charcoal was not observed and noted in the logs by the field geologists. While the detrital charcoal may exist in the subsurface, it does not appear to be widespread nor does it appear to be exerting an influence on chemical transport. As such, no change to our conceptual site model is necessary.

**DTSC Comment No. 2 -** Page 6, second bullet. Vertical hydraulic gradients are caused by pumping and not by the degree of confinement. It is usual in most alluvial basins for the degree of confinement to gradually increase with depth. In the Coastal Plain, the four main divisions of the alluvium correlate to Sierra glaciations, and it would not be surprising to find much of the same sequence in the smaller basins. The section should be revised to remove the relation of unconfined conditions to vertical gradient. In an

<sup>&</sup>lt;sup>1</sup> NASA. 2007. *Technical Memorandum: Additional Investigation Results*. Prepared by Battelle for the National Aeronautics and Space Administration. January.

<sup>&</sup>lt;sup>2</sup> NASA. 2003. *JPL Groundwater Modeling Report*. December.

<sup>&</sup>lt;sup>3</sup> Foster Wheeler Environmental Corporation (FWEC). 1999. Final Remedial Investigation Report for Operable Units 1 and 3: On Site and Off-Site Groundwater. August.

alluvial fan environment, new channels characteristically cut across soil horizons, so the assumption that these layers are intact is not supported.

## NASA's Response:

It is believed that the vertical gradients are caused by a combination of pumping, the lithology (individual silt beds), and vertical anisotropy.<sup>2,3</sup>

DTSC Comment No. 3 - Inspection of topography reveals a slightly more complex situation than described. The base of the San Gabriel Mountains has several fans centered on prominent drainages. In the Monk Hill basin, Flint Ridge blocks southern continuation of the fans, so the drainage upon the fans is shunted east to join the Arroyo. Because of the structure of the fans, water moving in buried channels tends to follow the same general pattern. It is more correct to say that groundwater gradients are more easterly, because of pumping. The actual particle flow direction is determined by the vector sum of the gradient vector and the anisotropy vector. Pumpage is not the most significant determinant of groundwater flow. The most important factor is topography, and water in the basins does flow from higher to lower elevations. The second most important factor is anisotropy, because it is an aquifer property, and pumping vectors are third, because they are superimposed on the other two factors. The section should be revised.

## NASA's Response:

Groundwater flow at JPL is complex and is affected by several factors, most significantly bedrock topography and pumping. Bedrock topography and pumping strongly influence the groundwater elevations near JPL. Data collected during the remedial investigation (RI) and the JPL modeling effort indicate that, in the vicinity of JPL, bedrock topography (see Figure R2 in the general response) and pumping have the greatest impact on groundwater flow paths. The RI<sup>4</sup> states that groundwater elevations fluctuated vertically up to 75 feet per year beneath JPL, primarily due to pumping of nearby municipal production wells and the amount of groundwater recharge from the Arroyo Seco spreading basins. The effect of pumping on groundwater flow in the vicinity of JPL is classified as significant, as evidenced by hydrographs and the groundwater-elevation contour maps presented in the RI. Data indicate that when municipal production wells are pumping, the water-table in the vicinity of the wells continuously declines until the wells are shut off; when the wells are shut off, water levels rise immediately. Information collected during the large-scale aquifer test (documented as an appendix in the JPL Groundwater Modeling Report<sup>5</sup>) conducted to supplement the JPL groundwater modeling effort further supports the significant effect operation of the municipal production wells (Ventura Well, Windsor Well, and Well 52) has on groundwater levels in the vicinity of JPL. While lateral anisotropy, resulting in preferential pathways, likely exists at a small scale near JPL due to the depositional environment in the Raymond Basin, these pathways do not significantly impact our understanding of groundwater flow at the scale of our study.

**DTSC Comment No. 4 -** Water resource models typically neglect the effect of lateral anisotropy because the bulk flow volumes are less affected. However, for certain transport problems, anisotropy cannot be neglected because the issue is determined by actual flow paths, not bulk movement. Thus, the RBMB model is not useful in predicting contaminant flow unless it incorporates horizontal anisotropy. Inspection of the particle tracks indicates it does not account for the north-south channel deposits of the Arroyo Seco, which indicates that the aquifer has been assumed to be laterally isotropic. This is not consistent with the depositional environment.

<sup>&</sup>lt;sup>4</sup> Foster Wheeler Environmental Corporation (FWEC). 1999. Final Remedial Investigation Report for Operable Units 1 and 3: On Site and Off-Site Groundwater. August.

<sup>&</sup>lt;sup>5</sup> NASA. 2003. JPL Groundwater Modeling Report. December.

NASA's Response: Data collected during the RI , the JPL modeling effort, and the RBMB modeling effort indicate that groundwater flow is primarily controlled by the bedrock surface and pumping, not the current location of the Arroyo Seco stream bed which is over 100 feet above the groundwater table in the Monk Hill Subarea. The bedrock surface channels groundwater flow southeast from JPL and then south as groundwater flows out of the Monk Hill Subarea. This is exactly what is predicted by the JPL and RBMB groundwater models.

DTSC Comment No. 5 – The methods used to calibrate the RBMB model are not described, nor are the actual values of conductivity, vertical anisotropy, or recharge used in its calibration. No water balance is provided. There is no way to evaluate whether unreasonable values or combinations of parameters were used to force matches with gradients. It is not stated whether automated parameter estimation was used. Since any one calibration is not unique, there is a range of values and combinations of parameters that will calibrate the model, yet some are more unlikely than others. The uncertainty of the calibration is not given. Likewise, no information on the JPL model was given other than the results. The results of the particle tracing indicate that both models assume laterally isotropic conditions. Basically, the models assume that basins are uniform layers of sand and silt/clays. The real basins, however, were laid down by streams flowing mainly north to south, and these stream channels create preferential southward flow pathways. The largest and most prominent of these is the Arroyo Seco. Any model that does not show the slightest deviation in particle tracks while crossing the Arroyo Seco sediments at right angles is not a believable model.

### **NASA's Response:**

It was not the intent of this document to provide a detailed description of the regional-scale RBMB model or the JPL model; a comprehensive discussion of model construction and calibration is provided in the respective modeling reports.<sup>2,6</sup> Model calibration is also discussed in these reports. The models were constructed using all of the available lithologic data, and did assume laterally isotropic conditions based on the depositional history and historical migration of the location of alluvial fans over time. Under these conditions, model calibration indicated accurate simulation of historical groundwater flow conditions. The JPL model also provides a detailed description of conditions near the mouth of the Arroyo Seco and the modeling approach that was chosen to represent these conditions.

**DTSC Comment No. 6 –** The northern boundary of the model is stated as the San Gabriel Mountains. The mountains are bounded by the Sierra Made Fault, a thrust fault that moves bedrock over alluvium. The geometry of the fault indicates that substantial alluvium extends beneath the fault to the north. It is not clear whether this alluvium was included in the model.

## NASA's Response:

The northern boundary of the model in the vicinity of JPL is the JPL Thrust Fault; alluvium beneath the fault is not included in the model.

**DTSC Comment No. 7 -** The water balance for the model needs to be shown, along with the interlayer water balances. Constant head boundaries have unlimited capacity to remove water from the basin, and errors in the subsurface outflow are often calibrated out by increasing both recharge and conductivity. General head boundaries, which limit outflow to the aquifer, conductants and gradient, are a better choice. Since a very large combination of flows and conductances can match the same gradient, inspection of outflow volumes is needed to identify whether reasonable outflow volumes are being produced by the

<sup>&</sup>lt;sup>6</sup> Geoscience. 2004. Technical Memorandum Raymond Basin Ground Water Flow Model Predictive Simulations. December.

boundary. Constant head boundaries are more appropriate to fully penetrating steams and lakes, and are not good choices for subsurface flow.

## NASA's Response:

A discussion of the water balance for the model is presented in the JPL Groundwater Modeling Report (see Section 2.7), and indicates that reasonable outflow volumes are associated with the boundary.

**DTSC Comment No. 8 -** Results of Groundwater Modeling. The flow fields of the two models are similar because they both assume the basins are laterally homogeneous and isotropic, which is obvious from the way the streamlines cross one major stream course after another without deflection. Neither model appears to incorporate anisotropy — a key feature of the aquifer that governs particle flows. The models do not accurately model contamination flow, only bulk flow. They are water resource models, not contaminant flow models. The particle tracks illustrate the gradient, but do not and cannot illustrate contaminant flow. The maps lack a north arrow and scale.

## NASA's Response:

The models were constructed using all of the available lithologic data, and did assume laterally isotropic conditions based on the depositional history and historical migration of the location of alluvial fans over time. Because the JPL model accurately represents the groundwater flow field, it can be used to show advective particle transport throughout the model domain. The JPL Model is appropriate for this study because plume containment has occurred with drinking water production wells operating in the Monk Hill Subarea since the early 1900s. The predicted groundwater flow field is supported in that particle tracking simulations performed with the JPL Model accurately recreated the extent of the existing carbon tetrachloride plume.

**DTSC Comment No. 9 -** It is unlikely that pumping in the Monk Hill basin contains JPL's contaminants, because the water would be forced to move upstructure and across grain to get to the wells. Real water follows the path of least resistance, and the actual flow paths tend to follow the structure of the fans. In anisotropic media, true particle paths diverge from hydraulic head maps because of the sideways component of conductivity. One characteristic of anisotropic aquifers is that contaminant plumes follow the topography, not the groundwater gradient.

#### **NASA's Response:**

The extent of carbon tetrachloride and groundwater-level elevation maps support a south/southeast groundwater flow direction in the vicinity of the JPL facility, consistent with the JPL Model.

**DTSC Comment No. 10 –** Figures 2 and 3. Over much of these two maps, particle tracks across topography at high angles. Under these scenarios, there is no real source of water to the Arroyo Seco near the Rose Bowl. There is no outflow to the southwest near South Pasadena either, yet Arroyo sediments clearly underlie the 110 Freeway alignment. There are no groundwater monitoring wells within the Arroyo south of Devil's Gate which forms a significant data gap. Recent personal communications with the LA Dept. of Public Works indicate perchlorate was detected during dewatering near the 110 Freeway, down the Arroyo Seco Channel.

#### **NASA's Response:**

The groundwater flow field used to generate the particle tracking figures is consistent with that historically observed in the Raymond Basin. Data collected during the RI, the JPL modeling effort, and the RBMB

modeling effort indicate that groundwater flow is controlled by the bedrock surface and pumping, not the current location of the Arroyo Seco stream bed. The bedrock surface channels groundwater flow southeast from JPL and then south as groundwater flows out of the Monk Hill Subarea. Recharge from the San Rafael Hills is a source of water to the Arroyo Seco near the Rose Bowl.

The linear distance from JPL (source area) to the 110 is approximately 6.3 miles (outside our study area), so perchlorate detected near the 110 Freeway further supports multiple sources of perchlorate in the area.

**DTSC Comment No. 11 -** The rate of groundwater movement is not well supported because the model uses boundaries liable to cause conductance errors. The models do not prove that contaminants were contained in the Monk Hill basin, only that there was a flattened gradient.

## NASA's Response:

The groundwater flow field predicted by the models is consistent with that historically observed in the Raymond Basin.

DTSC Comment No. 12 - Groundwater Geochemistry, page 12, last bullet (artificial recharge). Who made the estimate? Was it verified? Has the percentage been constant over time? The California Dept. of Water Resources observes that the use of dishwashers and automatic washers has changed the proportion of water used inside and outside of the home. The introduction of low-flow toilets has also skewed proportions. Because this recharge is a significant portion of the basin's water, errors in this value will propagate as conductivity errors in the model. Changes in the percentage of sewered areas also change areal recharge. It is also not clear whether proportion of delivered water to sewer flows were checked over time, which can lead to errors in estimating recharge.

#### **NASA's Response:**

A detailed discussion of the JPL model water budget is provided in Section 2.7 of the JPL Groundwater Modeling Report.<sup>2</sup> It is understood that there is a degree of uncertainty in estimating the return flow from applied waters and leaky distribution pipes, although these estimates were made using all available resources at the time of model construction. It should be noted that as stated in the JPL modeling report, the extent of unsewered areas has not changed substantially over time, and few changes have been made to the sewer system since 1963.

DTSC Comment No. 13 - Page 14, last bullet. The evidence for ion exchange is that sodium shows a wide range, and increases as calcium and magnesium decrease, generally by twice the amount, since sodium is monovalent and calcium and magnesium are divalent. The lower left triangle on the Piper shows that both Type 1 and Type 2 waters are softened by ion exchange, and Type 3 is not. Type 2 water appears to be simply a softened version of Type 1 native water. There appear to be two types of Type 3 water, particularly evident in the left lower triangle as distinct bands. These appear to be mixtures of Type 2 and Type 3 waters. No stability calculations are presented, but it is likely that Type 3 waters are nearly saturated with respect to calcium sulfate, and precipitation of calcium sulfate can skew the proportion of calcium to magnesium. Some analyses seem to have unusually high magnesium proportions, which suggest some calcium has been precipitated.

It has been reported<sup>7</sup> that an ion-exchange process could be responsible for the softening of the Type 1 water and thus creating Type 2 water in the deepest portions of the Raymond Basin aquifer. NASA's Additional Investigation did not focus on understanding the origin of Type 2 water because these waters have extremely low to non-detectable perchlorate and chlorinated organics, and because this water is relatively isolated from Types 1 and 3 water based on hydrochemical characteristics. The primary focus of the geochemistry evaluation in the Additional Investigation was understanding the impact of injection and the infiltration of imported water. The geochemical processes of ion exchange, mineral precipitation and dissolution, and mixing all take place at stratigraphically shallower levels than the Type 2 water zone. Type 3 water has no known interactions with Type 2 water because of their stratigraphic separation, which is supported by distinct hydrochemical differences and the general absence of dissolved perchlorate.

Mixtures of different types of water are present in the subsurface. However, it should be kept in mind that the different water types are ad hoc groupings based on broad distinctions in water compositions, and that there is no clear boundary between Types 1 and 3, and Types 1 and 2. Piper plots show that there is a continuum of all of the different types of water existing at this site (see Figure 5 of the Additional Investigation Technical Memorandum<sup>1</sup>).

During the Additional Investigation, NASA determined that Type 3 water is slightly oversaturated with calcite, as a result of calcium desorption from clay minerals in the unsaturated zone as sodium-rich imported water infiltrated through the soil. Type 1 water tends to be near the saturation level or slightly oversaturated. The presumed reason for calcite oversaturation is that ion exchange in the unsaturated zone is causing calcium-enriched water infiltrating from the surface to mix with carbonate-saturated aquifer water and precipitate calcite. Similar equilibrium calculations were performed to investigate groundwater saturation with respect to calcium sulfate (gypsum). When compared to the groundwater chemistry data, it can be seen that Type 1 water is undersaturated with respect to gypsum by approximately four orders of magnitude. However, Type 3 water tends to be undersaturated within a factor of 10, and a few data points almost fall on the gypsum solubility curve. These results signify that Type 3 water is strongly influenced by sulfate coming directly from the Colorado River. However, Type 3 water remains understaturated with respect to gypsum at every sampling location, and therefore we conclude that gypsum does not influence groundwater composition to a great extent throughout the Raymond Basin. Rather, as already has been demonstrated, calcite precipitation has the most significant effect on calcium levels in groundwater throughout the Basin.

**DTSC Comment No. 14 -** There are alternative ways of interpreting the Piper diagram if precipitation has occurred. It is not obvious that ion exchange has been properly accounted for in the analysis. What is shown as a maxing line in the lower triangle is obviously an ion exchange line.

## NASA's Response:

See response to DTSC Comment No. 13.

**DTSC Comment No. 15 -** Another factor not included in the analysis is the impact of percolated wastewater and sulfate/nitrate reduction. Sulfate reduction causes a shift in the proportion of sulfate to bicarbonate that looks like a mixing line, but is actually a removal line. Water mixed with wastewater is often softened and loses much of its sulfate. These reactions, however, are not really mixing phenomena. In any case, saturation indices need to be checked before mixing is invoked to explain the data. Yet another factor is whether some native water derived from metasediments near Flintridge also have high sulfate. An

<sup>&</sup>lt;sup>7</sup> Geoscience. 2004. Baseline Groundwater Assessment of the Raymond Basin Final Report, February

analysis of nitrate would be instructive, particularly if waters low in sulfate but high in chloride are also low in nitrate. This would suggest denitrification in addition to sulfate reduction.

## NASA's Response:

The oxidation-reduction (redox) conditions in the aquifer would not support sulfate reduction or denitrification. This statement is supported by elevated dissolved oxygen (DO) concentrations and high oxidation reduction potential (ORP) readings, elevated nitrate levels, relatively low total organic carbon (TOC) (electron donor) concentrations, and data indicating that other reductive processes are not occurring (e.g., iron reduction, sulfate reduction, and trichloroethylene [TCE]/tetrachloroethylene [PCE] reduction). The notable exception to this assessment is MW-20 (Screens 4 and 5). Although the DO concentrations are elevated and iron reducing conditions were not detected in MW-20 (Screens 4 and 5), the ORP readings were negative, nitrate was not present, and sulfide was detected in Screen 4 (potentially associated with sulfate reduction). These observations associated with deep water in MW-20 may signify that reducing conditions exist in this area.

**DTSC Comment No. 16 -** Aerobic conditions are assumed, yet much of the chemistry suggests local anaerobic conditions.

## NASA's Response:

After evaluating all terminal electron accepting parameters, the level of dissolved oxygen in the groundwater was used as the primary means of determining the redox conditions. The evaluation of the DO and ORP at the site showed that the aquifer is under aerobic conditions; however, inconsistencies in the groundwater data were observed in the deeper portions of MW-20. Nevertheless, the predominant terminal electron acceptor at the site is oxygen. The combination of the other terminal electron acceptors, specifically nitrate and ferrous iron, was used to support the dissolved oxygen levels. With respect to MW-20 at the lower depths, the negative ORP values may indicate a localized reduced zone. Note that if anaerobic conditions sufficient to reduce nitrate were established near MW-20, they likely also support reduction of perchlorate.

**DTSC Comment No. 17 -** While Figures 7 and 8 may suggest recharge along the western corridor, the particle tracking maps certainly do not, and in fact, the conspicuous absence of a groundwater mound associated with the Golf Course is a strong argument for anisotropic conditions beneath the Arroyo.

## NASA's Response:

Data collected during the RI, the JPL modeling effort, and the RBMB modeling effort indicate that groundwater flow is primarily controlled by the bedrock surface (see general response Figure R2) and pumping, not the current location of the Arroyo Seco stream bed, which is over 100 feet above the groundwater table near JPL. No monitoring wells are located in the Golf Course to evaluate the presence or absence of a groundwater mound.

**DTSC Comment No. 18 -** Figure 8 also shows that sulfate migrates along the Arroyo and its buried earlier channels. Note the similarity of the Ventura to the Copelin wells, and the Arroyo to the Sunset wells. The chemistry appears to track the geologic structure.

Figure 8 shows that sulfate levels in 1950 were relatively low and relatively consistent throughout the basin.

**DTSC Comment No. 19 -** Figure 9 only reinforces the impression that groundwater moves down the Arroyo. The conspicuous data gap in the Arroyo only serves to suggest that more data would probably show that sulfate is high near the Rose Bowl, and that in fact, despite the direction of the gradient, contaminant transport is respecting the geology.

## NASA's Response:

No data exist to demonstrate sulfate migration along the Arroyo. Sulfate data in the production wells is consistent with NASA's conceptual site model and groundwater modeling predictions by the RBMB groundwater model.

**DTSC Comment No. 20 -** Page 19. A table with estimated pound of perchlorate by source, and levels achieved by different dilutions would be welcome here. Using the perchlorate levels in Las Vegas wash to imply high levels in Colorado River water is not justified, and would, in any case, have a high degree of uncertainty. While the resultant wide distribution of background perchlorate smog in the basin exists, local sources greater than background can easily be distinguished.

## NASA's Response:

Data do not exist to create the requested table.

**DTSC Comment No. 21 -** [Groundwater ] Isotope Data. The chart shows just as much mixing of Type 3 water as it does of Types 1 and 2 waters. This graph suggests that the deep water is not necessarily old, unmixed water, but is just ion exchange native water, possibly with some sulfate reduction.

## NASA's Response:

NASA acknowledged in the Additional Investigation Technical Memorandum<sup>1</sup> that there was considerable variability and overlap in the  $\delta 1^8 O/\delta^2 H$  isotope compositions of the different water types. This is likely due to seasonal variability in the isotopic composition of local meteoric water and imported water.

Note that the  $\delta^{18}$ O/ $\delta^2$ H isotope data are not being used in the technical memorandum to classify water types, nor should they be (the water types are based on an extensive database of information spanning multiple decades). Rather, the point is made that Type 3 water is isotopically lighter on average relative to Types 1 and 2 water and lies below the Global Meteoric Water Line. This observation is consistent with other Los Angeles area studies associated with mixing between local meteoric water and imported Metropolitan Water District (MWD) water, which is lighter due to its inland origin.

**DTSC Comment No. 22 -** The strontium isotope analysis also suggests that Type 3 water is actually two different types, and that Type 1 water can be turned into Type 2 water by ion exchange. This was actually also shown on the Piper diagrams, but was misinterpreted.

#### NASA's Response:

See response to DTSC Comment No. 13.

**DTSC Comment No. 23 –** Tritium Samples. Although the data are not shown, it is likely that most of the Type 2 water is young, not old, which suggests that the old, deep water is simply in a part of the aquifer that cannot be mobilized by wells. Often this happens in anisotropic aquifers where wells are at right angles to the stream fabric, and where the actual source of water is upstream and downstream, not across the stream fabric.

## NASA's Response:

Tritium (<sup>3</sup>H or T) data are presented in Attachment 1 of the Additional Investigation Technical Memorandum.<sup>1</sup> Tritium is a part of the water molecule and therefore undergoes advective and diffusive transport in the same manner as bulk water. Tritium concentration (activity) is a useful parameter for assessing the mean age of water for periods of up to 60 years, due to its relatively short half-life of 12.4 years. Radioactive decay (beta emission) is commonly measured in Tritium Units (TU), where 1 TU = 1 T per 10<sup>18</sup> hydrogen atoms per liter of water.

Prior to 1952, the tritium level in the precipitation was approximate 2 TU in the LA Basin due to natural processes. During this period, an aquifer in the Basin undergoing continual recharge would have contained 2 TU, or less, due to mixing and average age of the water. Without further input of tritium, levels in the aquifer would have decayed down to 0.1 TU by year 2000 (approximately 4 half-lives). Thus, submodern waters are characterized by having very low tritium levels. In the nuclear bomb testing era, beginning in 1952, atmospheric tritium rose to a maximum in 1963, then quickly declined due primarily to mixing, and secondarily to natural radioactive decay. It is significant to note that the transfer of tritium from the atmosphere to surface water took place to a greater extent in the continental region of the US, and to a lesser extent in coastal regions.<sup>8</sup> As a consequence, rivers and lakes in the continent were enriched in tritium during fallout events, compared to water bodies near the coasts.

The complexity of mixing that takes place in most aquifers and the uncertainty regarding when infiltration occurred, combined with decay of the target analyte, make rigorous calculation of age nearly impossible in most circumstances. Therefore, investigators<sup>9</sup> have attempted to generalize the age of water based on relative levels of tritium. In *coastal and low latitude regions*, age can be estimated as follows:

- <0.8 TU, Submodern-recharged prior to 1952
- 0.8 to ~2 TU, Mixture between submodern and recent recharge
- 2 to 8 TU, Modern (<5 to 10 yrs)
- 10 to 20, TU Residual "bomb" tritium present
- >20 TU, considerable component of recharge from 1960s to 1970s

Tritium data measured for wells that carry Type 2 groundwater (MW-17 [Screen 5], MW-18 [Screen 5], MW-20 [Screen 5], and MW-24 [Screens 4 and 5]) have TU values less than 0.8 indicating submodern water, recharged prior to 1952. (Note MW-17 [Screen 5] tritium level was 0.865 TU, indicating some minor degree of mixture with more modern water).

**DTSC Comment No. 24 -** Carbon Tetrachloride. Contrary to the statement in the report, PCE and TCE make excellent tracers when their molar rations, not their absolute levels, are compared. Comparing and contrasting molar rations is very successfully used to differentiate solvent sources. The presence of PCE and TCE at the Sunset wells, despite the assertion that the Monk Hill pumping depression prevents JPL's plumes from migrating south, is a logical inconsistency.

<sup>&</sup>lt;sup>8</sup> United States Geological Survey (USGS). 2003. *Geohydrology, Geochemistry, and Ground-Water Simulation-Optimization of the Central and West Coast Basins, Los Angeles County, California*. Water-Resources Investigations Report 03-4065.

<sup>&</sup>lt;sup>9</sup> Clark, I. and P. Fritz. 1997. *Environmental Isotopes in Hydrogeology*. 1<sup>st</sup> edition.

**NASA's Response:** With the sources of PCE and TCE occurring offsite, cross-gradient, and west of JPL, the use of PCE to TCE ratios would not be appropriate in that no reference ratio could be established. In addition, one cannot connect PCE and TCE concentrations in Sunset Reservoir wells to JPL since other sources exist in the basin. It is because no other sources of carbon tetrachloride are present in the Monk Hill Subarea that make its use as a tracer possible.

DTSC Comment No. 25 - While carbon tetrachloride has not been detected in the Sunset wells, onsite monitoring data indicated it is breaking down to chloroform, despite assertions that it is not biodegrading. MW-3 Screen 2 shows both carbon-tet and chloroform, its first daughter product. While many people assume methylene chloride is a laboratory contaminant, in the presence of carbon-tet and chloroform, this is not justified. Sorption on natural carob is also a possible process attenuating carbon-tet, but the presence of daughter products is a stronger argument than it is degraded before reaching the Sunset wells. The data contradict the statement that biodegradation is not occurring. The data also suggest that water is not, in fact, flowing backwards towards Monk Hill.

## NASA's Response:

NASA's analysis recognized that biotic and abiotic carbon tetrachloride degradation requires an anaerobic environment. Groundwater data collected from the JPL monitoring network provide strong evidence that an anaerobic environment capable of degrading carbon tetrachloride is not present. These data include DO levels near saturation, nitrate levels generally greater than 1 mg/L as NO<sub>3</sub>, ORP readings generally above 100 mV, the general absence of ferrous iron, and the absence of evidence of anaerobic degradation of TCE or PCE within the JPL chemical plume. The presence of chloroform, a daughter product of carbon tetrachloride degradation, cannot be used to indicate anaerobic degradation of carbon tetrachloride since chloroform was a compound used during historic laboratory operations at JPL<sup>12</sup> and is a disinfection byproduct.

**DTSC Comment No. 26 -** The model cannot be used to predict the extent of carbon tetrachloride, since it incorrectly predicts the distribution of sulfate and perchlorate.

### **NASA's Response:**

See previous responses.

**DTSC Comment No. 27 -** Perchlorate Isotope Analysis. The isotope analysis shows that the perchlorate at the Sunset wells is a mixture of two sources, JPL and Las Vegas. This is what would be expected from spreading imported water in the vicinity of the JPL plume, which migrates down buried stream channels to the Sunset Reservoir area. MW-25 is the only well with a convincing difference from a mixture of JPL and Las Vegas perchlorate, which suggests fertilizer as a source.

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<sup>&</sup>lt;sup>10</sup> Doong, R.A. and S.C. Wu 1992. "Reductive Dechlorination of Chlorinated Hydrocarbons in Aqueous Solutions Containing Ferrous and Sulfide ions." *Chemosphere* 24:1063-1075.

<sup>&</sup>lt;sup>11</sup> Interstate Technology and Regulatory Council (ITRC). 2005. A Systematic Approach to In Situ Bioremediation in Groundwater Including Decision Trees on In Situ Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate. Technology/Regulatory Guidelines ISB-8.

<sup>&</sup>lt;sup>12</sup> Foster Wheeler Environmental Corporation. 1999. *Final Remedial Investigation Report for Operable Unit 2: Potential On-Site Contaminant Source Areas*. National Aeronautics and Space Administration, Jet Propulsion Laboratory, Pasadena, CA. November.

## NASA's Response:

We do not agree with the interpretation presented. Two of the Sunset wells, Bangham Well and Garfield Well, cannot be explained by mixing of JPL and "Las Vegas" sources. NASA believes that the groundwater collected from the Sunset Well does not represent a mixture of other perchlorate sources and a JPL source due to its similarity to MW-19-2. The data strongly support a perchlorate source in MW-19-2 that is distinct from JPL and within the flow path from perchlorate sources cross-gradient and west of JPL to the Sunset Reservoir area. Therefore, the MW-19-2 and Sunset Well may contain perchlorate from the same source but not from JPL.

DTSC Comment No. 28 - The aquifer is very likely to contain detrital charcoal, and in substantial amounts. This substrate makes a very good locus for biodegradation, and may account for the degradation of carbon tetrachloride. Perchlorate is chemically similar to nitrate and sulfate, and is likely degraded under reducing conditions that may be widely scattered within the aquifer. The investigation did not consider the presence of detrital charcoal as a factor. Chemical evidence of reduction is generally a better indicator of reducing conditions than ORP or DO measurements, which can be contaminated by exposure to atmospheric oxygen by a deteriorated well seal. The functional genomics analysis does not take microenvironments into account.

## NASA's Response:

NASA reviewed all available boring logs near JPL and detrital charcoal was not noted in any of the logs by the field geologists. See response to DTSC Comment No. 16 for discussion of redox conditions in the aquifer. While the detrital charcoal may exist in the subsurface, it does not appear to be widespread nor does it appear to be exerting an influence on chemical transport.

**DTSC Comment No. 29 -** The Sunset wells are down-structure from JPL. The fact that they are crossgradient is nullified by the anisotropy of the aquifer. The isotopic data show that at least some of the perchlorate in the Sunset wells originated at JPL.

# NASA's Response:

See previous responses and the response to General Comment No. 5.

#### ATTACHMENT NO. 3: RESPONSES TO COMMENTS FROM THE CITY OF PASADENA

On January 31, 2007, the National Aeronautics and Space Administration (NASA) released a study¹ regarding the extent of perchlorate and other chemicals in groundwater originating from the Jet Propulsion Laboratory (JPL) site. The objectives of the study were to (1) evaluate the downgradient (southern) extent of chemicals originating from the JPL facility and (2) determine if the occurrence of perchlorate in the Sunset Reservoir area was associated with migration from the JPL facility. The City of Pasadena, with support from Geoscience Support Services, Inc. (Geoscience), reviewed the NASA report and submitted comments. Responses to the comments from Geoscience are provided below.

#### **GROUNDWATER MODELING**

**Geoscience Comment No. 1** – The NASA Technical Memorandum<sup>1</sup> used a future pumping scenario instead of historical pumping to make conclusions regarding movement of contaminated groundwater in the Monk Hill Subarea.

# NASA's Response:

NASA appreciates the Raymond Basin Ground Water Flow Model Predictive Simulation report and its associated pumping model output provided by Geoscience as part of its review of the Additional Investigation Technical Memorandum.<sup>1,2</sup>

As part of NASA's additional investigation, the JPL Model<sup>3</sup> was used in combination with the RBMB Model to evaluate groundwater flow. The JPL Model was designed specifically to evaluate groundwater flow in the Monk Hill Subarea (as opposed to the entire Raymond Basin) and is therefore the more accurate model for evaluating conditions in the Monk Hill Subarea. NASA did take into consideration several historical pumping scenarios using the JPL Model, as discussed in the technical memorandum.<sup>1</sup> The JPL Model shows that chemicals originating at JPL are contained within the Monk Hill Subarea by municipal production wells. These model results are corroborated by carbon tetrachloride data. As described in NASA's technical memorandum, carbon tetrachloride is unique to JPL within the Monk Hill Subarea and does not extend outside the Monk Hill, consistent with groundwater modeling predictions.

In addition, NASA reviewed the RBMB Groundwater Model output provided as Figure 2 in the comments received from Geoscience. Contrary to what Geoscience reports in its comments, their model output does not show that "particle tracks originating from the Sunset Reservoir wells backtrack to the JPL source area" as no particles originating from the Sunset Reservoir wells travel back through the JPL source area (Figure 2). Rather, NASA notes the following:

- The capture zones for Sunset and Copelin wells extend to the south of the JPL facility, and do not contain groundwater located within the JPL boundary. Of the five Sunset Reservoir wells, Sunset and Copelin have had the highest levels of perchlorate. These results are consistent with previous results presented in NASA's technical memorandum.
- The capture zones for the Bangham, Garfield, and Villa wells cannot be discerned from the model output provided by Geoscience; however, the particle tracking lines do not appear to intersect the JPL facility.

<sup>&</sup>lt;sup>1</sup> NASA. 2007. *Technical Memorandum: Additional Investigation Results*. Prepared by Battelle for the National Aeronautics and Space Administration. January.

<sup>&</sup>lt;sup>2</sup> Note: NASA requested the Raymond Basin Management Board (RBMB) Groundwater Model in November 2006 to evaluate different pumping scenarios; however, the RBMB did not respond.

<sup>&</sup>lt;sup>3</sup> NASA. 2003. JPL Groundwater Modeling Report. December.

Other data presented in NASA's technical memorandum do not support perchlorate concentrations in the Bangham, Garfield, and Villa wells originating from JPL. Specifically, the JPL Groundwater Model and chemical data show that chemicals originating from JPL are contained within the Monk Hill Subarea. In addition, these three production wells have had the lowest levels of perchlorate of five Sunset Reservoir wells, and perchlorate isotope data show that the Bangham and Garfield wells have a different isotopic composition than JPL perchlorate (samples were not collected from Villa well because is was not in operation at the time).

Given the future pumping scenario, with backward tracking from 2024 to 2003, used in the RBMB Groundwater Model, NASA welcomes the opportunity to conduct forward particle tracking using the RBMB Groundwater Model, releasing particles from the JPL source area. NASA also would be interested in conducting forward particle tracking using the RBMB transient model, which is calibrated to the historical period spanning from 1981-2002. These approaches may help to further clarify the transport of chemicals originating from JPL. Furthermore, the approaches will address the differences between a historical pumping scenario and a future pumping scenario when using the RBMB model as well as provide other data points within the modeling study.

**Geoscience Comment No. 2** – Particle tracking models do not take into account hydrodynamic dispersion (i.e., spreading of plumes).

## NASA's Response:

NASA understands that the particle tracking simulations do not take into account hydrodynamic dispersion, which may show a larger plume footprint in the absence of plume containment. Several lines of evidence show that plume containment has occurred and advective particle tracking does provide a general idea of the area that is expected to be contained by the extraction wells under advective flow, which is similar to what can be expected of perchlorate migration due to its chemical properties. According to the Geoscience report, dispersivity, retardation and biodegradation are transport factors lacking in an advective transport model. Given the aerobic conditions prevalent throughout the aquifer, biodegradation of perchlorate is not expected. Furthermore, the retardation factor for perchlorate is negligible due to its chemical properties.

**Geoscience Comment No. 3** – The southern limit of JPL's perchlorate plume is not adequately characterized.

### **NASA's Response:**

Significant data exist to define the southern limit of JPL's perchlorate plume. Specifically, data collected from MW-20, MW-19, MW-21, and MW-26 indicate that the extent of perchlorate originating from JPL is contained within the Monk Hill Subarea, with MW-20 representing the southeastern extent of the plume. The hypothesis that groundwater originating from the JPL source area may have traveled south to MW-21 sometime in the past is not supported by the available data. First, MW-21 is clearly connected to flow cross-gradient and west of JPL (i.e., from La Cañada-Flintridge) based on both the RBMB and JPL groundwater models. Consistent with the groundwater models, the groundwater geochemistry shows a strong Type 3 water quality and elevated tritium levels, connecting the groundwater in MW-21 to injection of imported water in the Valley Water Company (VWC) wells. In addition, no carbon tetrachloride has ever been detected in MW-21 (while it has been in MW-10 and MW-5). Therefore, the southern limit of JPL perchlorate is adequately defined by evaluating all of the available data.

#### **GROUNDWATER GEOCHEMISTRY**

**Geoscience Comment No. 1** – The NASA technical memorandum does not adequately characterize chemical constituents of imported water used in the Raymond Basin.

# NASA's Response:

The chemical constituents of imported water used in the Raymond Basin were characterized and included in Attachment 2 of the technical memorandum.<sup>1</sup> The Piper plot in Attachment 2 depicts MWD (Weymouth Plant) cation/anion data obtained between 1976 and 2003. The Foothill Municipal Water District (FMWD) and Pasadena Water and Power (PWP) receive their water from the Weymouth Plant, and these data are representative of a mixture of Colorado River Water and State Project Water. In addition, State Water Project water (represented by the Jensen Plant) has a cation/anion composition that is similar to Colorado River water (see Figure A3-1), but significantly different from local water quality.

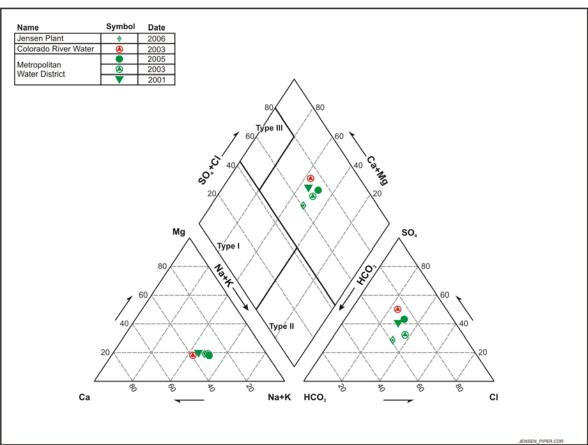


Figure A3-1. This Piper plot shows that imported water from the Colorado River and State Water Project has a similar cation/anion composition, which is significantly different from local water (Types 1 and 2).

**Geoscience Comment No. 2** – The NASA technical memorandum claims of imported water impacts on ambient water quality are not supported by data.

## NASA's Response:

Imported water does impact ambient water quality. As explained in the technical memorandum, Type 1 groundwater is characteristic of native groundwater in the Raymond Basin with calcium as the dominant cation and bicarbonate as the dominant anion. In contrast, Type 3 is not native, and is derived from introduction of imported water into the aquifer. Type 3 groundwater is characterized with calcium as the dominant cation and bicarbonate as the dominate anion, but with relatively elevated levels of chloride, sulfate, and total dissolved solids (TDS). There are several ways in which imported water reaches the aquifer, including irrigation, leaking distribution lines, artificial recharge, and direct injection. However, Type 3 water cannot be explained by simple mixing of Type 1 water with imported MWD water. The mechanism for producing Type 3 water involves sodium-calcium ion exchange between imported water and calcium-enriched clay minerals in the aquifer matrix, followed by mixing with Type 1 groundwater.

Concentrations of calcium and sodium in Monk Hill Subarea groundwater are shown graphically in Figure A3-2, where it can be seen that Type 3 groundwater typically has much higher calcium concentrations than Type 1 groundwater. This figure also shows that calcium concentrations in Type 3 groundwater are higher than those of either imported MWD water or the Colorado River water. Another difference in water quality is that imported MWD and Colorado River water have higher sodium content than either Type 1 or Type 3 groundwater (Figure A3-2). A mass action equation describing the ion exchange is shown by Eq. 1

$$2Na^{+}_{(aq)} + CaX_2 + Ca^{+2}_{(aq)} + 2NaX$$
 (1)

where X represents a cation-exchangeable substrate, such as a smectite or montmorillonite clay mineral. Smectite and illite/smectite mixed-layer clays are common weathering products of arkosic sands that make up the Basin alluvium.<sup>4</sup> The stoichiometry of Eq. 1 indicates that 2 moles of sodium (from the imported water) are exchanged for 1 mole of calcium (on the exchange sites).

Imported MWD water and Colorado River water also contains higher levels of sulfate and TDS. Figure A3-3 shows the sulfate and sodium concentrations in Type 1 and 3 groundwater, Colorado River, MWD, and Jensen waters. Anions, like sulfate, are not affected by ion exchange in soils, so the evolution of sulfate between Type 1 and Type 3 is based primarily on mixing. To raise sulfate concentration in Type 3 groundwater to levels where they are today, mixing must have occurred involving Type 1 groundwater with a high-sulfate source (e.g., Colorado River water). In summary, the ion-exchange processes discussed above and in the technical memorandum explain the mechanisms of how the imported water impacted the ambient water to increase the calcium and TDS concentrations and produce Type 3 groundwater.

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<sup>&</sup>lt;sup>4</sup> California Deptartment of Conservation. 1986. "Geology of the North Half of the Pasadena Quadrangle, Los Angeles County, California." Open-File Report 86-4 LA.

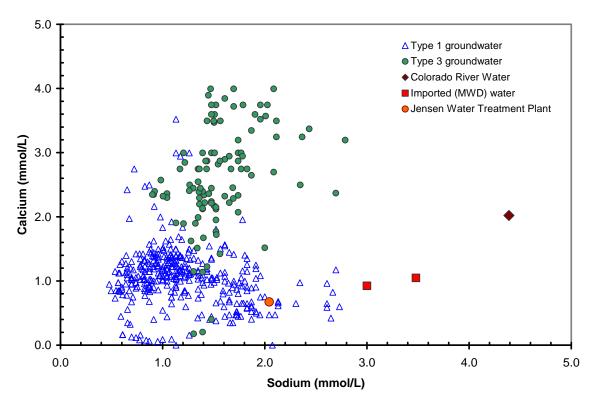


Figure A3-2. The distribution of calcium and sodium in Type 1 and Type 3 groundwaters in the Monk Hill Subarea substantiate the ion exchange reaction that results in Type 3 water.

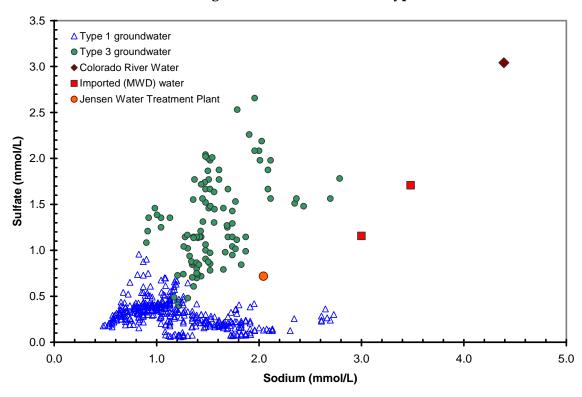


Figure A3-3. The distribution of sulfate and sodium in Type 1 and Type 3 groundwaters in the Monk Hill Subarea illustrates that higher sulfate concentrations in Type 3 water are derived from mixing Type 1 groundwater with a high sulfate source, such as Colorado River water.

**Geoscience Comment No. 3** – The NASA technical memorandum does not take into account vertical variations in water quality.

## NASA's Response:

NASA considered the vertical screening intervals for all monitoring locations independently, especially the depth-discrete locations in the 14 JPL multi-port monitoring wells when evaluating geochemistry, chemical concentrations, and isotopes. As the Remedial Investigation (RI) and the technical memorandum explain, vertical variations in water quality are related to the groundwater type (1, 2, or 3). Figure 10 in the technical memorandum shows the depth-discrete locations for the multi-port monitoring wells and illustrates how the depth has impacted the groundwater type. Furthermore, NASA specifically installed two new multi-port monitoring wells (MW-25 and MW-26) as part of the additional investigation to evaluate vertical variations in water quality. MW-25 is located near the Sunset Reservoir. In summary, NASA recognized the vertical variations in water quality and included them in the data analysis.

**Geoscience Comment No. 4** – Valley Water Company wells contradict NASA's technical memorandum water types.

## NASA's Response:

Geochemical data prior to the late 1980s are not available for the VWC wells. Understanding the evolution of water types in these wells since importation of MWD water began in the 1940s is not possible. There are data supporting the influence of imported water on the groundwater geochemistry in the VWC wells which is convincing:

- Attachment 2 of NASA's technical memorandum includes Piper diagrams for all four VWC wells. These diagrams demonstrate the ion exchange and mixing relationships between Type 1 and 3 waters and imported MWD water, which are described in NASA's technical memorandum (and depicted in Figure 6 of the technical memorandum). The VWC wells provide much to our understanding of water type evolution since the imported water was injected directly into these wells and therefore the ion exchange and mixing processes can be observed over time.
- The graphs provided by Geoscience associated with the VWC wells (Figures 10-13, 19-22, and 28-31) show elevated sulfate, chloride, and TDS levels consistent with NASA's interpretation of influence of imported MWD water on local water quality.
- NASA agrees that it is interesting that the limited water chemistry data available for the VWC wells prior to 1994 already show a strong influence from imported water. However, the water chemistry of the two La Cañada Irrigation District (LCID) wells, located immediately upgradient (within 500 feet) of the VWC wells, show a Type 1 classification in the late 1980s (see Figure A3-4). In addition, the water quality in LCID wells moves toward a Type 3 classification by the late 1990s, evidently influenced by water injected into the VWC wells.

In summary, the VWC well data support NASA's technical memorandum water type categorization.

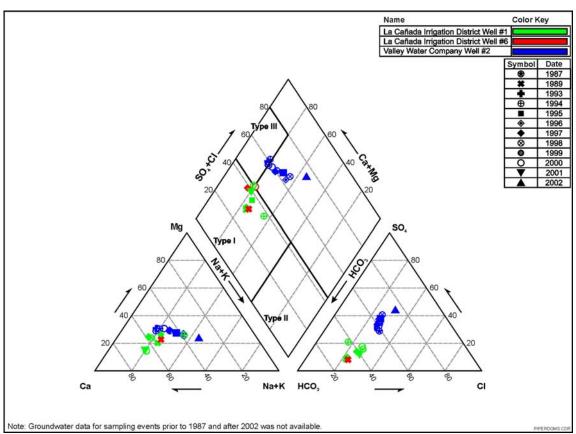


Figure A3-4. LCID wells are located immediately upgradient of the VWC wells, but are dramatically different in terms of water quality, thus supporting NASA's understanding of water quality in the VWC wells being strongly associated with injected MWD water.

**Geoscience Comment No. 5** – There are no consistent trends in sulfate in the Sunset Reservoir or Valley Water Company wells.

### NASA's Response:

Water has been imported to the Raymond Basin since the early 1940s. NASA interpretations associated with sulfate and the changes in water quality associated with imported water are based on data going back to the 1930s. Geoscience limited its sulfate trend analysis to the last 25 years (i.e., data available since the early 1980s) by which time significant impacts of imported water on the Raymond Basin had already occurred. Therefore, the trend analysis presented by Geoscience is of limited value.

**Geoscience Comment No. 6** –  $\delta^{18}$ O/ $\delta^{2}$ H isotope data are not consistent with regard to classification of water types.

#### NASA's Response:

NASA acknowledged in the technical memorandum that there was considerable variability and overlap in the  $\delta18O/\delta2H$  isotope compositions of the different water types. This is likely due to seasonal variability in the isotopic composition of local meteoric water and imported water.

It is important to note that the  $\delta^{18}$ O/ $\delta^{2}$ H isotope data are not being used in the technical memorandum to classify water types, nor should they be (the water types are based on an extensive database of cation/anion data spanning multiple decades). Rather, the point is made that Type 3 water is isotopically lighter on

average relative to Type 1 and 2 water and lies below the Global Meteoric Water Line. This observation is consistent with other Los Angeles area studies associated with mixing between local meteoric water and imported MWD water.

**Geoscience Comment No. 7** – Use of tritium isotopes contradicts classification by other methods.

## NASA's Response:

Geoscience's comment ignores the effect of transport time (and therefore the radioactive decay of tritium) between MW-19 or MW-21 and the Sunset Reservoir wells. That is, water with higher levels of tritium in the Monk Hill (such as those observed in MW-19 and MW-21) would have a much lower tritium level by the time it traveled to the Sunset Reservoir wells due to the radioactive decay. It is precisely because the radioactive decay rate for tritium is known that tritium can be used for age dating. The elevated tritium levels in MW-19 and MW-21 correlate with our understanding of the influence of water injected into the VWC wells.

**Geoscience Comment No. 8** – The NASA technical memorandum data on strontium shows a wide range of values that are inconclusive.

## NASA's Response:

NASA's interpretation of strontium isotopes supports our understanding of the geochemistry within the study area, and serves as a secondary line of evidence to support our conceptual model. Note that the strontium isotope data are not being used in the technical memorandum to classify water types (the water types are based on extensive data spanning multiple decades); however, they support our understanding of the water types. Conclusions from this study must be made by looking at all of the data together, and not in isolation.

#### **GROUNDWATER CHEMICAL CONCENTRATIONS**

**Geoscience Comment No. 1** – The conclusions in the NASA technical memorandum regarding the association of carbon tetrachloride and perchlorate are not supported by data and do not take into account the different fate and transport of the two chemicals.

### NASA's Response:

NASA's conclusions regarding the association of carbon tetrachloride and perchlorate are supported by available data and do take into account the different fate and transport of the two chemicals. Given the above comment, it is important to ensure that Geosciences better understand groundwater flow, geochemistry, and sources of perchlorate. Each well specifically mentioned in Geoscience's comment is addressed below:

- MW-6, MW-14, and MW-22: These wells are located on the western portion of the JPL facility, generally cross-gradient of the source area. Therefore, chemicals originating from the JPL source area would not be expected to flow past these wells. This understanding of groundwater flow is consistent with the absence of carbon tetrachloride in these wells (except for one isolated detection in MW-6 in 1993 of  $2.1~\mu g/L$ ). In addition, water typing for these three wells is predominantly Type 3, consistent with cross-gradient/non-JPL water. Taken together the data support the conclusion that perchlorate in these wells did not originate from the JPL source area.
- MW-16, MW-17, MW-19, MW-20, MW-21, and MW-24: These wells were discussed in detail within the technical memorandum. In summary, perchlorate in MW-16, MW-24, and MW-17 are believed

to be associated with a JPL source. The perchlorate in MW-19, MW-20 (Screens 1 and 2), and MW-21 are not believed to be associated with a JPL source. These interpretations are confirmed by multiple lines of evidence including groundwater modeling, the presence/absence of carbon tetrachloride, geochemical data, and perchlorate isotope results.

- MW-11: This well is interesting in that it has not had detections of perchlorate, but has had intermittent detections of carbon tetrachloride (in the second and third screened intervals).
- MW-1, MW-9, and MW-15: These wells are relatively shallow wells, located at the mouth of the Arroyo Seco and representative of subsurface flow from the San Gabriel Mountains. Carbon tetrachloride and perchlorate have not been detected in these wells (except for one isolated perchlorate detection in MW-15, 4.1 μg/L in May 2005).

As addressed specifically in the technical memorandum, NASA understands the differences in the fate and transport of perchlorate and carbon tetrachloride. Given the aerobic conditions prevalent throughout the aquifer, biodegradation of carbon tetrachloride and perchlorate is not expected. Furthermore, the retardation factors for carbon tetrachloride and perchlorate are negligible given the low levels of organic carbon associated with the aquifer sediment and the anionic nature of perchlorate. Therefore, the use of carbon tetrachloride as a tracer for perchlorate at the JPL site is reasonable.

**Geoscience Comment No. 2** – The NASA technical memorandum does not correctly estimate the amount of Colorado River Water imported into the Raymond Basin

# NASA's Response:

NASA recognizes that the source of imported water from MWD into the Raymond Basin is a blend of waters. As such, the mass of perchlorate was estimated conservatively based on the amount of water imported from the Colorado River not on the total amount of imported water. The volume of imported Colorado River was estimated as follows:

- 1952-1971: Imported water volumes were taken from Watermaster Reports. It was assumed that all of the water was from the Colorado River, since the State Water Project was not completed until 1972. This time period accounts for nearly half of the estimate, 452,500 ac-ft.
- 1972-1975: Imported water volumes were taken from Watermaster Reports. No data were available to estimate the contributions from the Colorado River, so an estimate of 65% Colorado River water was used. This time period accounts for 65,600 ac-ft of the estimate.
- 1976-2002: Imported water volumes were taken from Watermaster Reports. The contribution from the Colorado River was estimated based on total MWD usage of Colorado River and State Water Project water during those years. These data were obtained from MWD's 2005 Regional Urban Water Management Plan.<sup>5</sup> During this time, the annual percentage of Colorado River water imported by MWD ranged from 40% to 87%. This time period accounts for another 451,000 ac-ft of Colorado River water.

Note that the perchlorate mass estimate of 3,000 lbs used in the technical memorandum is a hypothetical, conservative estimate (i.e., low since perchlorate concentrations in MWD water were likely higher than 5  $\mu$ g/L in the past). Even using this conservative estimate it illustrates that a large quantity of perchlorate was imported to the Basin.

**Geoscience Comment No. 3** – The NASA findings inferring Colorado River water is responsible for Sunset Reservoir wells' perchlorate is flawed.

<sup>&</sup>lt;sup>5</sup> Metropolitan Water District of Southern California (MWD). 2005. Regional Urban Water Management Plan. November.

# NASA's Response:

Sulfate can precipitate in the unsaturated zone as a fairly insoluble salt (e.g., gypsum or anhydrite) when water evaporates, whereas perchlorate salts are relatively soluble. Thus, sulfate and perchlorate will exhibit contrasting behavior when the evaporated salts are re-exposed to water. Perchlorate will be preferentially dissolved and transported downward with recharge. Therefore, the mechanism proposed by NASA is valid.

NASA concurs that Colorado River water could have a measurable effect on the perchlorate levels in the Raymond Basin as demonstrated by the Geoscience estimates presented in Table 2 of its comments. The Geoscience estimate does not take into account spatial variability in the dissolved perchlorate concentrations (for example perchlorate is detected in some screened intervals but not in others). The variability of the sulfate data within the Raymond Basin demonstrates that the mass of compounds associated with imported MWD water will not be uniformly mixed throughout the aquifer. In addition, perchlorate isotope data support that sources other than Colorado River water and JPL exist in the Basin (e.g., fertilizer source). Therefore, when the data from this study are examined holistically, the lines of evidence show that the perchlorate found in the Sunset Reservoir wells did not originate from a JPL source.

#### PERCHLORATE ISOTOPES

**Geoscience Comment No. 1** – The NASA technical memorandum did not measure the isotopic signature of perchlorate in imported water from MWD, and did not measure the isotopic signature of the perchlorate source material responsible for groundwater contamination in the JPL area.

## NASA's Response:

NASA agrees that perchlorate isotope analysis of imported MWD water may be valuable. However, the isotopic composition observed in the Las Vegas Wash and at the Basic Management and Industrial (BMI) site in Henderson, Nevada is believed to describe the perchlorate isotopic composition of the MWD water. The BMI site is recognized as the primary source of perchlorate in the river and it is unlikely that the surface water could support conditions necessary for anaerobic biodegradation (which could change the isotopic signature). A strong argument in support of the assumption that the perchlorate in the imported river water has the same isotopic composition as the Las Vegas Wash is that the perchlorate concentration in the imported Colorado River water decreased simultaneously with the groundwater cleanup at the BMI site.

NASA does not have perchlorate source material used at JPL in the 1940s-1950s. Regardless, we know the isotopic composition of perchlorate in the JPL source area groundwater and that it is maintained during transport. In addition, there is no evidence to suggest that the isotopic composition of the JPL source perchlorate has changed.

**Geoscience Comment No. 2** – Water quality data and functional genomics testing do not support the statement that "perchlorate degradation is likely not occurring at the site."

### **NASA's Response:**

NASA and Geoscience are in agreement that, in general, the redox conditions in the aquifer would not support biodegradation of perchlorate. This is supported by the dissolved oxygen concentrations and ORP readings, elevated nitrate levels, relatively low total organic carbon (TOC) (electron donor) concentrations, and data indicating that other reductive processes are not occurring (e.g., iron reduction, sulfate reduction, TCE/PCE reduction). The exception to this assessment is MW-20 (Screens 4 and 5). Although the DO

concentrations are elevated and iron reducing conditions were not detected in MW-20 (Screens 4 and 5), the ORP readings were negative, nitrate was not present, and sulfide was detected in Screen 4 (potentially associated with sulfate reduction). These observations associated with deep water in MW-20 may indicate that reducing conditions exist in the older, deeper water near this well. However, this water predates the introduction of perchlorate into the aquifer (e.g., deeper levels of MW-20 had tritium values less than 0.8 TU) and there was no perchlorate detected in the MW-20 (Screens 4 and 5) during the additional investigation. Most importantly, regardless of aquifer redox conditions at MW-20, the JPL perchlorate plume would not be impacted. Lastly, the perchlorate isotope data for the Sunset Reservoir wells do not exhibit a signature consistent with biodegradation of JPL perchlorate.<sup>6</sup>

With regard to the high DO levels, excess air in the range of values observed during the additional investigation is common in groundwater, especially in arid areas with thick unsaturated zones and rapid recharge events.<sup>7,8</sup> Thus there is no reason to believe that the high DO values are artifacts of faulty well construction.

With respect to the potential of perchlorate biodegradation, microcosm tests indicated that perchlorate could be degraded under laboratory conditions using the indigenous soil microbial population from JPL.9 The microbe responsible for perchlorate degradation at JPL was identified as *Dechlorosoma suillum* strain JPLRND. Positive results for the chlorite dismutase (cld) gene throughout the site were expected as microcosm tests already indicated that perchlorate could be degraded under laboratory conditions. The positive results of cld mRNA at MW-1 could be associated with naturally occurring perchlorate present throughout the southwestern United States, <sup>10</sup> although perchlorate has never been detected in this well. The positive results of the cld mRNA at MW-24 are likely associated with the OU-1 treatment system that extracts groundwater, removes perchlorate using an anaerobic fluidized bed reactor (FBR), and then reinjects the treated water.

Lastly, regarding the use of perchlorate isotope data to distinguish between anthropogenic sources, Dr. Sturchio prepared a technical memorandum (dated May 15, 2007 and is available at the JPL Web site: <a href="http://jplwater.nasa.gov">http://jplwater.nasa.gov</a>) that addresses application of perchlorate isotopes for distinguishing between synthetic sources.

<sup>6</sup> 

<sup>&</sup>lt;sup>6</sup> Sturchio, N.C., J.K. Böhlke, A.D. Beloso, S.H. Streger, L.J. Heraty and P.B. Hatzinger. 2007. "Oxygen and Chlorine Isotopic Fractionation During Perchlorate Biodegradation: Laboratory Results and Implications for Forensics and Natural Attenuation Studies." *Environmental Science and Technology* 41, 2796-2802.

<sup>&</sup>lt;sup>7</sup> Heaton, T.H.E., and J.C. Vogel. 1981, "Excess Air in Groundwater." *Jour. Hydrol.*, v. 50, 201-216.

<sup>&</sup>lt;sup>8</sup> Aeschbach-Hertig, W., F. Peeters, U. Beyerle, and R. Kipfer. 1999. Interpretation of Dissolved Atmospheric Noble Gases in Natural Waters." *Water Resources. Res.* 35, 2779-2792.

<sup>&</sup>lt;sup>9</sup> Hatzinger, P.B., M.D. Whittier, C.W. Byran, and W.J. Guarini. 2002. "In-Site and Ex-Situ Bioremediation Options for Treating Perchlorate in Groundwater." *Remediation*, 12(2): 69-86.

<sup>&</sup>lt;sup>10</sup> Rao, B., T.A. Anderson, G.J. Orris, K.A. Rainwater, R. Srinath, R.M. Sandvig, B.R. Scanlon, D.A. Stonestrom, M.A. Walvoord, and W.A. Jackson. 2007. "Widespread Natural Perchlorate in Unsaturated Zones of the Southwest United States." *Environmental Science and Technology* 41, 4522-4528.

# ANALYTICAL METHODS AND QUALITY CONTROL

**Geoscience Comment No. 1** – There are several methods and quality control shortcomings in the water quality data

## NASA's Response:

NASA understands the observations about iron, dissolved organic content, sulfide content, conductivity, and electrical conductance analysis in groundwater. Even so, none of these measurements affects NASA's interpretations. All of the chemical analyses were performed by a certified laboratory. The conductivity and electrical conductance measurements were performed in the field, and used only to confirm that the groundwater parameters had stabilized and the water was ready for sample collection.

**Geoscience Comment No. 2** – The study does not provide adequate support for the analytical error associated with the stable perchlorate isotope method and the study did not conduct replicate sampling.

## NASA's Response:

The quoted errors of perchlorate isotopic analyses are not instrumental errors, as stated in the Geoscience comments, but instead are best estimates of the analytical precision of the entire method based on replicate analysis of standards in the laboratory, replicate analysis of extracted perchlorate, and field duplicates. The accuracy and precision of the method has been documented previously in other studies published in peer-reviewed venues. The method has been used to extract perchlorate from Chilean nitrate salts, and it has been tested with simulated salt solutions spiked with perchlorate isotopic reference materials, with excellent agreement. Other quality-assurance tests that have been performed, but not yet been published, will be presented in a manuscript that is currently in preparation for a peer-reviewed analytical chemistry journal. The method has been thoroughly tested and is proven to be reliable.

<sup>&</sup>lt;sup>11</sup> Sturchio, N.C., J.K. Böhlke, B. Gu, J. Horita, G.M. Brown, A. Beloso, Jr., L.J. Patterson, P.B. Hatzinger, W.A. Jackson, and J.R. Batista. 2006. "Stable Isotopic Composition of Chlorine and Oxygen in Synthetic and Natural Perchlorate." B. Gu, and J.D. Coates, eds., *Perchlorate- Environmental Occurrence, Interactions and Treatment*: Springer, New York, p. 93-109.

<sup>&</sup>lt;sup>12</sup> Böhlke, J.K., N.C. Sturchio, B. Gu, J. Horita, G.M. Brown, W.A. Jackson, J. Batista, P.B. Hatzinger, 2005. "Perchlorate Isotope Forensics." *Anal. Chem.* 7838-7842.